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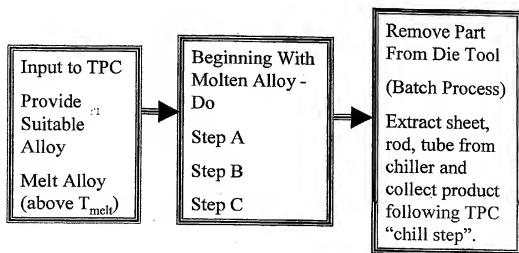
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(54) Title: THERMOPLASTIC CASTING OF AMORPHOUS ALLOYS



(57) Abstract: A process and apparatus for thermoplastic casting of a suitable glass forming alloy is provided. The method and apparatus comprising thermoplastic casting the alloy in either a continuous or batch process by maintaining the alloy at a temperature in a thermoplastic zone, which is below a temperature, T_{nose} (where, the resistance to crystallization is minimum) and above the glass transition temperature, T_g , during the shaping or moulding step, followed by a quenching step where the item is cooled to the ambient temperature. A product formed according to the thermoplastic casting process is also provided.



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

THERMOPLASTIC CASTING OF AMORPHOUS ALLOYS

FIELD OF THE INVENTION

This invention relates to novel methods of casting amorphous alloys, and, more particularly, to methods of thermoplastic casting such amorphous alloys.

BACKGROUND OF THE INVENTION

A large proportion of the metallic alloys in use today are processed by some form of solidification casting. In solidification casting the metallic alloy is melted and cast into a metal or ceramic mold, where it solidifies. The mold is then stripped away and the cast metallic piece is ready for use or for further processing. Commercial-scale casting processes are divided into two principal groups, expendable mold processes and permanent mold processes. In an expendable mold process, the mold is used only one time, such as in investment casting, which involves the use of refractory shells as molds. In a permanent mold process, metallic or graphite molds are repeatedly used for multiple castings.

Permanent molding processes can be classified by the type of mechanism used to fill the mold. In one form of permanent mold casting, the molten metal is fed to the mold under the force of gravity or a relatively small metal pressure head. In another form, referred to as die casting, the molten metal is supplied to the die-casting mold under a relatively high pressure, typically 500 psi (pounds per square inch) or more, such as with the aid of a hydraulic piston. In such a process the molten metal is forced into the shape defined by the interior surface of the mold. The shape can usually be more complex than that easily attained using permanent mold casting because the metal can be forced into the complexly shaped features of the die-casting mold, such as deep recesses. The die casting mold is usually a split-mold design such that the mold halves can be separated to expose the solidified article and facilitate the extraction of the solidified article from the mold.

1 High-speed die-casting machines have been developed to reduce
production costs, with the result that many of the small cast metallic parts found
in consumer and industrial goods are produced by die-casting. In such die-
5 casting machines a charge or "shot" of molten metal is heated above its melting
point and forced into the closed die under a piston pressure of at least several
thousand pounds per square inch. The metal quickly solidifies, the die halves are
opened, and the part is ejected. Commercial machines may employ multiple die
10 sets such that additional parts can be cast while the previously cast parts are
cooling and being removed from the die and the die is prepared with a lubricant
coating for its next use.

Although these methods have proven effective in making parts at
relatively high processing speeds, there are several problems inherent with these
15 techniques. For example, when the metal is forced into the die-casting mold in
commercial die-casting machinery it first solidifies against the opposing mold
walls. As a result, defects arising from turbulent flow at the surface of the die-
cast article are formed. Also, there is a tendency to form a shrinkage cavity or
20 porosity along the centerline of the die-casting mold when unsolidified liquid is
trapped inside a solid shell of solidified metal.

In addition, because the metal is fed into the die under high pressure and
at high velocities, the molten metal is in a turbulent state. Indeed, in many
25 applications an atomized "spray" of metal is used to fill the dies. This turbulent
action causes discontinuities, not only at the surface of the cast part, but also in
the center of the cast part from gas being trapped in the solidifying metal-
creating porosity. Atomization of the liquid metal also creates internal
30 boundaries within the part weakening the finished article. Accordingly, on the
whole die-casting produces rather porous parts of relatively low soundness, and
therefore having relatively poor mechanical properties. As a result, die-cast parts
are not usually used for applications requiring high mechanical strengths and
35 performance.

1 Amorphous alloys (glass forming alloys or metallic glass alloys) differ from
conventional crystalline alloys in their atomic structure, which lacks the typical
long-range ordered patterns of the atomic structure of conventional crystalline
5 alloys. Amorphous alloys are generally processed and formed by cooling a molten
alloy from above the melting temperature of the crystalline phase (or the
thermodynamic melting temperature) to below the "glass transition
temperature" of the amorphous phase at "sufficiently fast" cooling rates, such
10 that the nucleation and growth of alloy crystals is avoided. As such, the
processing methods for amorphous alloys have always been concerned with
quantifying the "sufficiently fast cooling rate", which is also referred to as
"critical cooling rate", to ensure formation of the amorphous phase.

15 The "critical cooling rates" for early amorphous alloys were extremely
high, on the order of 10^6 °C/sec. As such, conventional casting processes were not
suitable for such high cooling rates, and special casting processes such as melt
spinning and planar flow casting were developed. Due to the extremely short
time available (on the order of 10^{-3} seconds or less) for heat extraction from the
20 molten alloy, early amorphous alloys were also limited in size in at least one
dimension. For example, only very thin foils and ribbons (order of 25 microns in
thickness) were successfully produced using these conventional techniques.

25 Because the critical cooling rate requirements for these amorphous alloys
severely limits the size of parts made from amorphous alloys, the use of early
amorphous alloys in bulk objects and articles has been limited despite the many
superior properties of the amorphous alloy materials. Over the years it has been
determined that the "critical cooling rate" is a very strong function of the
30 chemical composition of amorphous alloys. (Herein, the term "composition"
includes incidental impurities such as oxygen in the amorphous alloy).
Accordingly, new alloy compositions with much lower critical cooling rates have
been sought.

35 In the last decade, several bulk-solidifying amorphous alloy (bulk-metallic
glass or bulk amorphous alloys) systems have been developed. Examples of such
alloys are given in U.S. Patent Nos. 5,288,344; 5,368,659; 5,618,359; and

1 5,735,975, each of which is incorporated herein by reference. These amorphous
alloy systems are characterized by critical cooling rates as low as a few
°C/second, which allows the processing and forming of much larger bulk
5 amorphous phase objects than were previously achievable.

With the availability of low "critical cooling rates" in bulk-solidifying
amorphous alloys, it has become possible to apply conventional casting processes
to form bulk articles having an amorphous phase. Using "heat flow" equations
and simple approximations, the critical cooling rate can be correlated to the
10 "critical casting dimension" of amorphous phase articles, i.e., the maximum
castable dimension for articles that retain an amorphous phase. For example,
the definition of "critical casting dimension" varies depending on the shape of the
amorphous phase article and in turn it becomes the maximum castable diameter
15 for long rods, the maximum castable thickness in plates, and the maximum
castable wall thickness in pipes and tubes.

In addition to their lower "critical cooling rate", bulk-solidifying
amorphous alloys have several additional properties that make their use in die
20 casting processes particularly advantageous, as described in U.S. Patent No.
5,711,363, which is incorporated herein by reference. For example, bulk-
solidifying amorphous alloys are often found adjacent to deep eutectic
compositions so that the temperatures involved in die-casting operations on
25 these materials are relatively low. Additionally, upon cooling from high
temperature, such alloys do not undergo a liquid-solid transformation in the
conventional sense of alloy solidification. Instead, the bulk-solidifying amorphous
alloys become more and more viscous with decreasing temperature, until their
viscosity is so high that, for most purposes, they behave as solids (although they
30 are often described as undercooled liquids). Because bulk-solidifying amorphous
alloys do not undergo a liquid-solid transformation, they do not experience a
sudden, discontinuous volume change at a solidification temperature. It is this
volume change that leads to most of the centerline shrinkage and porosity in die-
35 cast articles made of conventional alloys. As a result of its absence in bulk-
solidifying amorphous alloys, the die-cast articles produced with this material

1 are of higher metallurgical soundness and quality than conventional die-cast articles.

5 Even though, bulk-solidifying amorphous alloys provide some remedy to the fundamental deficiencies of solidification casting, and particularly to the die-casting and permanent mold casting processes, as discussed above, there are still issues which need to be addressed. First, there is a need to make still larger bulk objects, and articles of bulk-solidifying amorphous alloys, and also a need to make these articles from a broader range of alloy compositions. Presently
10 available bulk solidifying amorphous alloys with large critical casting dimensions are limited to a few groups of alloy compositions based on metals not necessarily optimized from either an engineering or cost perspective. Accordingly, there is a pressing need to overcome these compositional
15 limitations.

In the prior art of processing and forming bulk-solidifying amorphous alloys, the cooling of the molten alloy from above the thermodynamic melting temperature to below the glass transition temperature has been realized using a
20 single-step monotonous cooling operation. For example, metallic molds (made of copper, steel, tungsten, molybdenum, composites thereof, or other high conductivity materials) at ambient temperatures are utilized to facilitate and expedite heat extraction from the molten alloy. Accordingly, in the prior art, the correlation between the critical cooling rate and the "critical casting dimension"
25 is based on a single-step monotonous cooling process. As such, prior art processes put severe limitations on the "critical casting dimension", and are not suitable for forming larger bulk objects and articles of a broader range of bulk-solidifying amorphous alloys.
30

The single-step cooling operation of bulk-solidifying amorphous alloys also initiates the rapid formation of a solid shell against the opposing mold walls, due to the rapid temperature decrease from above the melting temperature down to
35 below glass transition temperature. This solidification shell impedes the flow of molten alloy adjacent to the mold surface and limits the replication of very fine die-features. As a result, it is often necessary to inject the molten alloy into the

1 dies at high-speed, and under high-pressure, to ensure sufficient alloy material is
introduced into the die prior to the solidification of the alloy, particularly in the
manufacture of complex and high-precision parts. Because the metal is fed into
5 the die under high pressure and at high velocities, such as in high-pressure die-
casting operation, the molten metal is in a turbulent state. Indeed, in many
applications an atomized "spray" of molten bulk-solidifying amorphous metal is
used to fill the dies. As in the high-pressure die-casting processes with
10 conventional materials, this turbulent action causes discontinuities, not only at
the surface of the cast part, but also in the center of the part from gas being
trapped in the solidifying metal-creating porosity. Atomization of the liquid
metal also creates internal boundaries within the part weakening the finished
article. Finally, the turbulent flow creates shear bands and serrations in the flow
15 pattern.

Accordingly, there is needed to find an improved approach to the casting of
amorphous metals which permits the rapid production, of large, high-quality,
high-precision, complex parts.

20 SUMMARY OF THE INVENTION

The invention is directed to both a thermoplastic casting process and to an
apparatus for implementing thermoplastic casting of suitable glass forming
25 alloys. Also included in the invention are articles of amorphous alloy made by the
inventive thermoplastic casting process.

In one embodiment, the invention is directed to a method and apparatus
for thermoplastically casting a bulk-solidifying amorphous alloy in a continuous
30 process by initially cooling the alloy (Step A) to an intermediate thermoplastic
forming temperature; and then thermalizing and maintaining the alloy
temperature at a near constant and uniform spatial profile in a molding step
(Step B), while simultaneously shaping and forming a product. Step B is then
35 followed by a final quenching step (Step C), where the final cast product is cooled
to ambient temperature. In such an embodiment, the thermoplastic forming
temperature is chosen to fall in a thermoplastic zone lying above the glass

1 transition temperature, whereby the rheological properties of the liquid can be
exploited to carry out alloy shaping and forming using practical pressures and on
time scales sufficiently short to avoid alloy crystallization.

5 In another embodiment, the thermoplastic casting uses a batch process.

In still another embodiment, the thermoplastic forming temperature used
in Step B lies above the glass transition but below a crystallization temperature,
 T_{nose} , where, T_{nose} is the temperature where crystallization is most rapid and
occurs in the shortest time scale. Below T_{nose} , the time available before
10 crystallization, $t_c(T)$, depends on temperature and steadily increases with
decreasing temperature. In such an embodiment, a suitable choice of
thermoplastic forming temperature allows for a sufficient molding time by
shifting the onset of crystallization to times much longer than the minimum
15 crystallization time, T_{nose} .

In yet another embodiment, the alloy is shaped in a heated mould or tool
die. In such an embodiment, the mould or tool die is preferably kept within 150
°C of the glass transition temperature of the alloy. In such an embodiment, the
20 liquid alloy equilibrates with the mould or tool die and achieves a nearly uniform
temperature equal to that of the mould or tool die. In one exemplary
embodiment, the mould or die is temperature controlled through a feedback
control system with both active cooling, such as a gas cooling system, and active
25 heating used to maintain a constant die temperature.

In still yet another embodiment, the temperature of the mould or tool die
in Step A is maintained within about 150 °C of T_g , and in Step B the
temperature of the mould or tool die is maintained within about 150 °C of T_g . In
30 one preferred embodiment of the current invention, the temperature of the
mould or tool die in Step A is maintained within about 50 °C of T_g , and in Step B
the temperature of the mould or tool die is maintained within about 50 °C of T_g .

In still yet another embodiment, the temperature of the mould or tool die
35 in Step A is maintained above the temperature of the mould or tool die in Step B.
In one preferred embodiment of the current invention, the temperature of the

1 mould or tool die in Step B is maintained above the temperature of the mould or
tool die in Step A.

5 In still yet another embodiment, the time spent in Step B is about 5 to 15
times more than the time spent in Step A. In one preferred embodiment, the
time spent in Step B is about 10 to 100 times more than the time spent in Step
A. In still another preferred embodiment, the time spent in Step B is about 50 to
500 times more than the time spent in Step A.

10 In still yet another embodiment, the pressure applied to the undercooled
melt in Step B is about 5 to 15 times more than the pressure applied to the
molten metal in Step A. In yet another embodiment, the pressure applied to the
undercooled melt in Step B is about 10 to 100 times more than the pressure
15 applied to the molten metal in Step A. In still another embodiment, the pressure
applied to the undercooled melt in Step B is about 50 to 500 times more than the
pressure applied to the molten metal in Step A.

20 In still yet another embodiment, the front end of the undercooled alloy is
introduced into a dog-tail tool in Step B, and thereafter this tool is utilized to
extract articles of the amorphous alloy continuously.

25 In still yet another alternative, however, the molten alloy is maintained in the
mould or tool die for a time suitable to achieve a nearly uniform melt
temperature equal to that of the mould. In one preferred embodiment the
moulding time is maintained between about 3 and 200 seconds, and more
preferably the time is between about 10 and 100 seconds.

30 In still yet another alternative, the rate of flow of liquid alloy through the
mould or die tool is maintained at a constant desired velocity or strain rate. In
one preferred embodiment the strain rate is held between about 0.1 and 100 s⁻¹.

35 In still yet another alternative embodiment, pressure is used to move the
molten alloy through the tool. In such an embodiment, the pressure is preferable
held to a value less than about 100 MPa, and more preferably to a value less
than about 10 MPa.

1 In still yet another embodiment, the invention the a mould or die tool is
any one of a permanent or expandable mould, a closed die or closed-cavity die,
and an open-cavity die.

5 In still yet another embodiment, the invention is directed to an extrusion
die capable of the continuous production of a two-dimensional amorphous alloy
product. In such an embodiment, the two dimensional product may be a sheet,
plate, rode, tube, etc. In one preferred embodiment, the product is a sheet or
10 plate having a thickness of up to about 2 cm or a tube having diameter up to
about 1 meter and a wall thickness of up to about 5 cm.

In still yet another embodiment, the invention is directed to a die tool for
the thermoplastic casting of glass alloys. In one such embodiment the die tool
includes an expansion zone where the melt is rapidly cooled past the
15 crystallization zone in a thin restricted cross sectional area, or heat exchanger,
which serves to cool the liquid sufficiently rapidly to bring the centerline
temperature below the crystallization "nose" at T_{nose} , and then the melt is
expanded into a portion of the tool of greater thickness. In such an embodiment,
20 the restricted zone preferably has a thickness from about 0.1 to 5 mm, and the
expanded zone has a thickness from about 1 mm to 5 cm.

In still yet another alternative embodiment of the invention, the die tool
has a roughened entrance surfaced to maintain melt contact and a polished exit
25 surface to permit boundary slip between the die and melt. In one such
embodiment, a lubricant is used in the exit to promote this slipping.

In still yet another embodiment, the expansion zone also contains a
roughened surface to promote non-slip of the melt. In one such embodiment the
30 expansion zone has a pitch angle of less than about 60 degrees and preferably
less than about 40 degrees.

In still yet another embodiment, the die is a split mould die which can be
opened to remove the final product.

35 In still yet another embodiment of the invention, the amorphous alloy is a
Zr-Ti alloy, where the sum of the Ti and Zr content is at least about 20 atomic
percent of the alloy. In a more preferred embodiment of the invention, the

1 amorphous alloy is a Zr-Ti-Nb-Ni-Cu-Be alloy, where sum of the Ti and Zr
content is at least about 40 atomic percent of the alloy. In another more
preferred embodiment of the invention, the amorphous alloy composition is a Zr-
5 Ti-Nb-Ni-Cu-Al alloy, where sum of the Ti and Zr content is at least about 40
atomic percent of the alloy.

In still yet another embodiment of the invention, the amorphous alloy is
an Fe-base, where Fe content is at least about 40 atomic percent of the alloy.

10 In still yet another embodiment, the provided amorphous alloy has a
critical cooling rate of about 1,000 °C/sec or less, and the heat exchanger has a
channel width less than about 1.5 mm. In another embodiment of the invention,
the provided amorphous alloy has a critical cooling rate of about 100 °C/sec or
less, and the heat exchanger has a channel width less than about 5.0 mm.

15 In still yet another embodiment, the invention is directed to a product
made by the thermoplastic casting process or apparatus. The product may be
any device including: a case for a watch, computer, cell phone, wireless internet
device or other electronic product; a medical device such as a knife, scalpel,
20 medical implant, orthodontics, etc.; or a sporting good such as a golf club, ski
component, tennis racket, baseball bat, SCUBA component, etc.

In still yet another embodiment, the invention is directed to an amorphous
alloy article wherein the critical cooling rate of the amorphous alloy composition
25 is about 1,000 °C or more, and the amorphous alloy article has a minimum
dimension of about 2 mm or more, and preferably about 5 mm or more, and still
more preferably about 10 mm or more.

30 In still yet another embodiment, the invention is directed to an amorphous
alloy article wherein the critical cooling rate of the amorphous alloy composition
is about 100 °C or more, and the amorphous alloy article has a maximum critical
casting thickness of dimension of about 6 mm or more, and preferably about 12
mm or more, and still more preferably about 25 mm or more.

35 In still yet another embodiment, the invention is directed to an amorphous
alloy article wherein the critical cooling rate of the amorphous alloy composition
is about 10 °C or more, and the amorphous alloy article has a maximum critical

1 casting dimension of about 20 mm or more, and preferably about 50 mm or more,
and still more preferably about 100 mm or more.

5 In still yet another embodiment, the invention is directed to an amorphous
alloy article wherein the amorphous alloy article comprises sections with an
aspect ratio of about 10 or more, and preferably with an aspect ratio of about 100
or more.

10 In still yet another embodiment the alloy product has an elastic limit of
more than about 1.5%, and more preferably more than about 1.8%, and still more
preferably an elastic limit of about 1.8 % and a bend ductility of at least about
1.0%.

In still yet another embodiment, the product has functional surface
features of less than about 10 microns in scale.

15 BRIEF DESCRIPTION OF THE DRAWINGS

These and other features and advantages of the present invention will be
better understood by reference to the following detailed description when
considered in conjunction with the accompanying drawings wherein:

20 FIG. 1 is a flow chart of an embodiment of a thermoplastic casting process
according to the current invention.

FIG. 2 is a graphical representation of a thermoplastic casting process
according to the current invention.

25 FIG. 3 is a graphical comparison of the crystallization properties of two
amorphous alloys. The diagram is referred to as a Time-Temperature-
Transformation diagram, and illustrates the time elapsed before the onset of
crystallization of the liquid at various undercooling temperatures.

30 FIG. 4a is an exemplary schematic diagram of a DSC scan for a first
exemplary amorphous alloy according to the present invention.

FIG. 4b is an exemplary schematic diagram of a DSC scan for a second
exemplary amorphous alloy according to the present invention.

35 FIG. 5 is a Time-Temperature-Transformation diagram of an amorphous
alloy according to the invention.

1 FIG. 6 is a graphical representation of the dependence of the properties of
amorphous alloys on strain rate vs. temperature.

5 FIG. 7 is a cross-sectional schematic diagram of a thermoplastic casting
apparatus according to one embodiment of the current invention.

 FIG. 8 is a graphical representation of the temperature vs. time history of
the liquid alloy flowing through a die tool at the centerline of the liquid.

 FIG. 9 is a graphical comparison of a thermoplastic casting process
according to the current invention vs. a conventional casting process.

10 FIG. 10 is a Time-Temperature-Transformation diagram of an amorphous
alloy according to the invention.

 FIG. 11 is a graphical representation of the dependence of the properties
of amorphous alloys on viscosity vs. temperature.

15 FIG. 12 is a cross-sectional schematic diagram of a thermoplastic casting
apparatus according to one embodiment of the current invention.

 FIG. 13 is a cross-sectional schematic diagram of a portion of a
thermoplastic casting apparatus according to one embodiment of the current
20 invention. The diagram illustrates the conditions required to maintain a non-slip
boundary condition at the interface between the melt and the die tool.

 FIG. 14 is a cross-sectional schematic diagram of an expansion section of a
thermoplastic casting apparatus according to one embodiment of the current
25 invention.

 FIG. 15 is a cross-sectional schematic diagram of a thermoplastic casting
apparatus according to one embodiment of the current invention. The apparatus
is used to make composite materials containing a mixture of an amorphous alloy
30 and a second material.

 FIG. 16 is a cross-sectional schematic diagram of a thermoplastic casting
apparatus according to one embodiment of the current invention. The apparatus
is used to make braided wires.

35 FIG. 17 is a cross-sectional schematic diagram of a thermoplastic casting
apparatus according to one embodiment of the current invention.

1 FIG. 18 is a cross-sectional schematic diagram of a heat exchanger section
of the thermoplastic casting apparatus according to one embodiment of the
current invention shown in FIG. 17.

5 DETAILED DESCRIPTION OF THE INVENTION

 The present invention is directed to a method and apparatus for
processing bulk metallic glasses (amorphous alloys) into unitized, high quality,
net shape parts by controlling the temperature, pressure, and strain rate of the
10 liquid amorphous alloy during processing to maintain the amorphous alloy in a
quasi-plastic state during shaping, the process being called thermoplastic casting
(TPC) herein.

 The invention relies on the observation that the time, $t_x(T)$, for
15 undercooled glass forming liquids to undergo crystallization varies
systematically and predictably as the liquid is cooled below the melting point of
the crystalline solid phase (or phase mixture), T_m , down to the glass transition
temperature, T_g , where the liquid alloy becomes a frozen solid.

 This variation in crystallization time is frequently described in
20 metallurgical literature by the use of time-temperature-crystal transformation
diagrams (TTT-diagrams) or by continuous-cooling-crystal transformation
diagrams (CCT-diagrams). In the present invention, we will focus on TTT-
25 diagrams. An exemplary schematic TTT-diagram is shown in FIG. 2. As shown,
the TTT-diagram is a plot of the time, $t_x(T)$, required to crystallize a prescribed
detectable volume fraction (typically ~5%) of the liquid at a given processing
temperature, T , in the undercooled liquid (between the T_m and T_g). The TTT-
30 diagram is directly measured by melting the liquid (above T_m), cooling relatively
quickly to the selected temperature, T , in the undercooled range, and then
measuring the time elapsed before crystallization begins. Such diagrams have
been measured for many glass forming alloys. The crystallization region of such
35 diagrams have a characteristic "C-shape".

 As shown in FIGs. 2 and 3, the time for crystallization exhibits a
minimum, which will simply be referred to as t_x , at a temperature called T_{nose}

1 lying somewhere midway between T_g and T_m . We refer to this minimum time as
a single representative parameter of the TTT-diagram given by $t_x(T)$, examples of
measurements of t_x will be given. Above or below T_{nose} , the time required for
5 crystallization increases rapidly. Thus, once cooled below T_{nose} , in a time scale
shorter than t_x , the time required to crystallize the liquid will increase with
decreasing temperature and will generally be much longer than t_x , allowing for
extended processing for times far beyond t_x without the risk of crystallization.

10 To process a liquid below T_{nose} , one must shape and form the liquid under
pressure or stress. The stress or pressure required depends on the rheological
properties of the liquid. Bulk metallic glass forming liquids remain quite fluid at
temperatures well below T_{nose} and can be formed and shaped with relatively low
pressures (e.g. 1-100 MPa) in practical time scales (1-300 seconds). The inventors
15 have surprisingly discovered that this characteristic can be exploited in a
solidification casting process, where a multi-step cooling operation is designed by
concurrently exploiting the characteristic "C"-shape of the bulk-solidifying
amorphous alloys. Measurements of viscosity and rheological properties of bulk
20 glass forming liquids, combined with data from the measured TTT-diagrams,
form the basis of practicing the invention. Specifically, The characteristic "C"-
shape of TTT-diagrams, combined with the temperature dependence of the
viscosity of glass forming liquids permits the design of processes which use a
25 multi-step temperature cooling history (as shown schematically in FIGs. 2 and 3)
to sequentially:

- (1) Avoid crystallization by cooling relatively quickly from above T_m to a
temperature, T , below T_{nose} thereby avoiding crystallization during
30 this initial cooling step;
- (2) Carry out thermoplastic forming and shaping operations at the
thermoplastic forming temperature, T , between T_g and T_{nose} using
modest pressures to form the liquid in convenient time scales which
avoid crystallization of the alloy at the thermoplastic forming
35 temperature. The process is carried out in a time scale shorter than
 $t_x(T)$; and

- 1 (3) Recover a substantially amorphous product by using a final cooling
step, which brings the product from the thermoplastic forming
temperature to ambient temperature.

5 The invention uses the detailed form of the TTT (Time-temperature-Transformation) diagrams. This form depends on the specific alloy to be processed. Further, the TTT-diagrams may show substantial variations even within alloys deemed to have the same or similar "critical cooling rates" or critical casting dimensions. More particularly, since the initial cooling step is
10 designed to avoid crystallization at the TTT-diagram nose, once this step is completed the forming operation is no longer limited by the minimum time to nucleation. As a result of this, the multiple step operations of this invention can be used to overcome the "critical casting dimension" limitation of a single step
15 process. This results in the ability to cast thicker sections of a given amorphous alloy than would be permitted by a single step casting operation. In other words, the process of this invention allows one to overcome previously perceived critical dimension limits that arise when one casts to an ambient temperature mold in a single step monotonous cooling process. This multi-step process allows one to
20 expand critical casting dimensions for a given glass-forming alloy. It can be used to enhance processability of otherwise marginal glass forming liquids and significantly expands the range of amorphous metals that can be used in
25 practical applications.

Further, the invention also recognizes that by controlling the pressure and/or strain-rate profile at certain temperature ranges, amorphous alloys can be formed and shaped into higher quality articles having much higher aspect-ratios
30 with closer tolerances and far more detailed replication of mold features. In sum, the process allows production of very high quality, precision substantially amorphous net shape components having exceptional soundness, integrity, and mechanical properties. Herein "substantially amorphous" is defined as a final
35 as-cast article having at least 50% by volume of the article having an amorphous atomic structure, and preferably at least 90% by volume of the article having an amorphous atomic structure, and most preferably at least 99% by volume of the

1 article having an amorphous atomic structure. The detailed basis for these
conclusions will become clear through the use of specific examples and preferred
embodiments of the process presented below.

5 One embodiment of the basic method of the current invention is shown in
a flow-chart in FIG. 1, and graphically in FIG. 2. In a first step, a suitable bulk-
solidifying alloy is first melted above its thermodynamic melting temperature
(T_m) forming a molten supply of amorphous alloy. Although specific examples of
10 amorphous alloys will be discussed in the current application, it should be
understood that any bulk-solidifying or bulk-metallic glass alloy which may be
stabilized in a thermoplastic forming zone upon cooling between the
crystallization nose, T_{nose} , and the glass transition temperature, T_g , and
15 maintained in this thermoplastic state for sufficient time to process the alloy,
may be utilized in the current invention. Exemplary embodiments of such bulk-
solidifying amorphous alloys have been described, for example, in U.S. Pat. Nos.
5,288,344 and 5,368,659, whose disclosures are incorporated herein by reference.

20 Following initial heating and melting, the molten alloy is introduced into
the casting machine and processed in three steps. In Step A, the temperature of
the molten metal is rapidly quenched until the temperature of alloy is lower than
the alloy's critical crystallization temperature, T_{nose} , but higher than the alloy's
glass transition temperature, T_g . As discussed above, this temperature range is
25 referred to as the "thermoplastic zone" of the alloy. Examples of the "nose" in the
TTT-diagram (see FIGs. 2, 3, and 5).

30 In Step B, the temperature of the alloy is maintained in the thermoplastic
zone for a time sufficient to shape the metal as desired. However, this shaping
time must be sufficiently short to avoid the onset of crystallization. Again, as
discussed above, using the TTT-diagrams (e.g., FIGs. 2, 3, and 5) for a specific
material, one can define an available time prior to the onset of crystallization,
 $t_x(T)$, at thermoplastic temperature, T . The process time must be less than this
35 time.

Finally, in Step C, the temperature of the alloy is quenched from the
thermoplastic temperature to a temperature near the ambient temperature such

1 that a fully hardened solid part is produced. After the quenching or final "chill"
process, the hardened product is either removed from the die for a batch-
processed piece, or extracted in a continuous casting process.

5 FIGs. 2 and 3 schematically show exemplary Time-Temperature-
Transformation diagrams for crystallization (TTT-diagrams) of a hypothetical
liquid alloy during the thermoplastic casting process. In both these figures, the
TTT-diagram is overlaid with the method steps described above. The TTT-
10 diagrams show the well-known crystallization behavior of the liquid alloy when
it is undercooled below its equilibrium melting point T_{melt} . As discussed briefly
above, it is well known that if the temperature of an amorphous alloy is dropped
below the melting temperature the alloy will ultimately crystallize if not
15 quenched to the glass transition temperature before the elapsed time exceeds a
critical value, $t_c(T)$. This critical value is given by the TTT-diagram and depends
on the undercooled temperature. However, there is a process window or
thermoplastic window below the temperature, T_{nose} , and above the solid glass
region and in the process according to the present invention, the alloy is initially
20 cooled sufficiently rapidly from above the melting point to this thermoplastic
temperature (below T_{nose}) to bypass the nose region of the material's TTT-
diagram (T_{nose} , which represents the temperature for which the minimum time to
crystallization of the alloy will occur) and avoid crystallization.

25 For a given alloy strain rate or injection velocity, there is also a minimum
thermoplastic processing temperature required to avoid instabilities in the flow
pattern such as shear bands. In a preferred embodiment of the present
invention, the thermoplastic process temperature is chosen to lie above this
30 minimum temperature for flow instability. Thus, Step A, comprises: (1) injecting
the molten alloy into a mould tool held at a thermoplastic process temperature;
(2) ensuring by suitable choice of the die tool, that the melt is everywhere (from
surface to centerline) cooled sufficiently rapidly to avoid crystallization as it is
35 cooled past the crystallization "nose" at T_{nose} ; and (3) choosing a final
thermoplastic process temperature high enough to avoid melt flow instabilities
such as shear banding. The alloy is then held at the thermoplastic processing

1 temperature for Step B, this step being the molding or shaping step. Step B
occurs at a thermoplastic processing temperature and must take place in a time
short enough to avoid crystallization at this temperature. As described above,
5 this time, $t_K(T)$, is determined by the TTT-diagram. As shown in FIG. 3,
although any bulk metallic glass may be used, the rate at which the liquid
temperature must be lowered to avoid crystallization at T_{nose} in Step A, and the
length of time the alloy can be maintained in the thermoplastic region and
processed in Step B, ultimately depends on the TTT-diagram of the chosen alloy,
10 and specifically on the form of the curve, $t_K(T)$.

For example, a Zr-Ti-Ni-Cu-Be based amorphous alloy made by
Liquidmetal Technologies under the tradename Vitreloy-1 can be processed in
the thermoplastic temperature range, up to a factor of 10 longer than a marginal
15 amorphous alloy (such as a Cu-Ti-Ni-Zr base Vitreloy-101 also made by
Liquidmetal Technologies), and this process time can be expanded even further
using other amorphous alloys, such as those made by Liquidmetal Technologies
under the tradenames Vitreloy-4 and Vitreloy-1b, for example. Likewise, the
20 cooling rate required in Step A to reach the thermoplastic temperature from the
high temperature melt depends on the minimum crystallization time, t_K ,
observed at the crystallization "nose". Thus, the critical cooling history
requirements in both Step A and Step B depend on the details of the TTT-
25 diagram of a particular alloy.

Although embodiments utilizing Vitreloy series alloys are discussed above,
any bulk-solidifying amorphous alloy may be utilized in the present invention, in
a preferred embodiment the bulk-solidifying amorphous alloy has the capability
30 of showing a glass transition in a Differential Scanning Calorimetry (DSC) scan.
Further, the feedstock of bulk-solidifying amorphous alloy preferably has a ΔT_{sc}
(supercooled liquid region) of more than about 30 °C as determined by DSC
measurements at 20 °C/min, and preferably a ΔT_{sc} of more than about 60 °C,
35 and still most preferably a ΔT_{sc} of about 90 °C or more. One suitable alloy
having a ΔT_{sc} of more than about 90 °C is $Zr_{47}Ti_{18}Ni_{10}Cu_{7.5}Be_{27.5}$. U.S. Patent
Nos. 5,288,344; 5,368,659; 5,618,359; 5,032,196; and 5,735,975 (each of which are

1 incorporated by reference herein) disclose families of such bulk solidifying
amorphous alloys with ΔT_{sc} of about 30 °C or more. Herein, ΔT_{sc} is defined as
the difference of T_x (the onset of crystallization) and T_g (the onset of glass
5 transition) as determined from standard DSC scans at 20 °C/min.

One such family of suitable bulk solidifying amorphous alloys may be
described in general terms as $(Zr, Ti)_a(Ni, Cu, Fe)_b(Be, Al, Si, B)_c$, where a is in the
range of from about 30% to 75% of the total composition in atomic percentage, b
is in the range of from about 5% to 60% of the total composition in atomic
10 percentage, and c is in the range of from about 0% to 50% in total composition in
atomic percentage.

Another set of bulk-solidifying amorphous alloys are ferrous metals, such
as Fe, Ni, and Co based compositions. Examples of such compositions are
15 disclosed in U.S. Patent No. 6,325,868; Japanese Patent Application No.
200012677 (Publ. No. 20001303218A), and publications to A. Inoue, *et al.* (Appl.
Phys. Lett., Volume 71, p. 464 (1997)) and Shen, *et al.* (Mater. Trans., JIM,
Volume 42, p. 2136 (2001)), all of which are incorporated herein by reference.

20 One exemplary composition of such alloys is $Fe_{72}Al_5Ga_2P_{11}Ce_6B_4$. Another
exemplary composition of such alloys is $Fe_{72}Al_7Zr_{10}Mo_6W_2B_{15}$. Although these
alloy compositions are not processable to the degree of the above-cited Zr-base
alloy systems, they can still be processed in thicknesses around 1.0 mm or more,
25 sufficient to be utilized in the current invention.

In general, crystalline precipitates in bulk amorphous alloys are highly
detrimental to their properties, especially to the toughness and strength, and as
such generally preferred to a minimum volume fraction possible. However, there
30 are cases in which, ductile crystalline phases precipitate in-situ during the
processing of bulk amorphous alloys, which are indeed beneficial to the
properties of bulk amorphous alloys, and particularly to the toughness and
ductility of such alloys. Such bulk amorphous alloys comprising such beneficial
precipitates are also included in the current invention. One exemplary case is
35 disclosed in (C.C. Hays et. al, Physical Review Letters, Vol. 84, p 2901, 2000).

Further, the selection of preferred compositions of bulk amorphous alloys can be tailored with the aid of the general crystallization behavior of the bulk-solidifying amorphous alloy. For example, in a typical DSC heating scan of bulk solidifying amorphous alloys, crystallization can take one or more steps. The preferred bulk-solidifying amorphous alloys are ones with a single crystallization step in a typical DSC heating scan. However, most of the bulk solidifying amorphous alloys crystallize in more than one step.

Shown schematically in FIG. 4a is one type of crystallization behavior of a bulk-solidifying amorphous alloy in a DSC scan. (For the purposes of this disclosure all the DSC heating scans are carried out at the rate of 20 °C/min and all the extracted values are from DSC scans at 20 °C/min. Other heating rates such as 40 °C/min, or 10 °C/min can also be utilized while the basic physics of this disclosure still remaining intact.)

In this example, the crystallization occurs over two steps. The first crystallization step occurs over a relatively large temperature range with a relatively slower peak transformation rate, whereas the second crystallization step occurs over a smaller temperature range than the first and at a much faster peak transformation rate than the first. Here ΔT_1 and ΔT_2 are defined as the temperature ranges over which the first and second crystallization steps respectively occur. ΔT_1 and ΔT_2 can be calculated by taking the difference between the onset of the crystallization and the "outset" of the crystallization, which are calculated in a similar manner for T_x , by taking the cross section point of the preceding and following trend lines as depicted in FIG. 4a. ΔH_1 and ΔH_2 can also be calculated by calculating the peak heat flow value compared to the baseline heat flow value. (It should be noted that although the absolute values of ΔT_1 , ΔT_2 , ΔH_1 and ΔH_2 depend on the specific DSC set-up, and the size of the test specimens used, the relative scaling (i.e. ΔT_1 vs ΔT_2) should remain intact).

Shown schematically in FIG. 4b is another type of crystallization behavior of a bulk-solidifying amorphous alloy in a typical DSC scan at the heating rate of 20° C/min. Again the crystallization occurs over two steps, however, in this

1 example the first crystallization step occurs over a relatively small temperature
range with a relatively faster peak transformation rate, whereas the second
crystallization occurs over a larger temperature range than the first and at a
5 much slower peak transformation rate than the first. Again, here ΔT_1 , ΔT_2 , ΔH_1
and ΔH_2 are defined and calculated as described above.

A sharpness ratio can be defined for each crystallization step by taking the
ratio $\Delta H_N / \Delta T_N$. The higher $\Delta H_1 / \Delta T_1$ compared to the other ratio, e.g., $\Delta H_N /$
10 ΔT_N , the more preferred the alloy composition is. Accordingly, from a given
family of bulk solidifying amorphous alloys, the preferred composition is the one
with the highest $\Delta H_1 / \Delta T_1$ compared to the other crystallization steps. For
example, a preferred alloy composition has $\Delta H_1 / \Delta T_1 > 2.0 * \Delta H_2 / \Delta T_2$. Still
15 more preferable is $\Delta H_1 / \Delta T_1 > 4.0 * \Delta H_2 / \Delta T_2$. For the two cases described
above, the bulk-solidifying amorphous alloy with the second crystallization
behavior (as shown in FIG. 4b) is the preferred alloy for more aggressive
thermoplastic casting, i.e. for operations to produce components with higher
aspect ratios and finer features.

20 Although materials having only two crystallization steps are shown above,
the crystallization behavior of some bulk solidifying amorphous alloys can take
place in more than two steps. In such cases, the subsequent steps, i.e., ΔT_3 , ΔT_4
... ΔH_N and ΔH_3 , ΔH_4 ... ΔH_N can also be defined. In such cases, the preferred
25 compositions of bulk amorphous alloys are ones where ΔH_1 is the largest of ΔH_1 ,
 ΔH_2 , ... ΔH_N .

Accordingly, the range of metallic glass formulations which can be
processed is only limited by the processability of the available glass
30 compositions, processability being determined by the time temperature
transformation (TTT, i.e., FIGs. 2 and 3) diagram or continuous cooling
transformation diagram (CCT) of the material. There is no requirement as to the
dimensional limitations for components such as plates, sheets, rods and other
35 parts, which arise from the ability to avoid crystallization. The TPC process can
be altered to overcome such dimensional limitations by using expansion sections

1 and heat exchangers (as shown in FIGs. 12, 14, and 17), thereby increasing the critical casting thickness of glass forming alloy plates.

It should be understood that the TTT-diagrams in FIGs. 2 and 3 are shown schematically, and that although it appears from these diagrams that one could keep the alloy within the thermoplastic region indefinitely without crystallization occurring, it should be understood that the crystallization process has only been slowed in this region because of the increased viscosity of the alloy material, and that if held long enough at this "thermoplastic temperature" the alloy would eventually crystallize. (See for example the experimentally measured TTT-diagram in FIG. 5 showing the crystallization region and times before crystallization for an experimental Zr-based alloy.) However, although crystallization will eventually occur, even for alloys held in this thermoplastic region, the time allowed for processing is greatly expanded, allowing for the controlled casting of many different products with complex shapes and geometric features, and with very large aspect ratios.

This ability to process for longer times is important because, as shown in FIG. 6, if the alloy is injected into the mold at too high a velocity or strain rate, here taken as an average liquid strain rate in s^{-1} in the channel, the alloy will behave as an inhomogeneous non-Newtonian liquid, and will thus be subject to inhomogeneities, such as shear banding or atomization. In this case, strain rate can be defined as the typical velocity of the liquid along the centerline of a flow channel divided by the width or diameter of the flow channel. Accordingly, in order to ensure high-quality parts, the alloy must be injected into the mold at rates below those that result in non-Newtonian flow and instability, i.e., in a Laminar flow regime, where a Laminar flow regime (or Newtonian flow regime) is characterized by uniform and stable streamlines for the flow.

The transition to non-Newtonian flow and instability depends on the viscosity and the temperature of the alloy as well. Table I, below, shows the minimum temperatures required for specific strain rates to avoid non-Newtonian flow and instabilities in the flow patterns. Table I also gives the pressure required to achieve the given strain rates at the minimum temperature.

Table I: Process Conditions (Strain Rate vs. Temperature), for Vitreloy 1		
Strain Rate Control (s ⁻¹)	Temperature (°C)	Stress Levels (MPa)
0.1	Down to 400 °C	Up to 10-30 MPa
1.0	Down to 430 °C	Up to 15-20 MPa
10	Down to 450 °C	Up to 20-30 MPa

Likewise, the strain rate, the temperature used, and the TTT-diagram of the material will determine the time available for processing and the maximum aspect ratio (L/D) of the part achievable, as summarized below in Table II. The values in Table II were calculated using parameters measured for Vitreloy 1.

Table II: Formability of Components, Vitreloy-1			
Strain Rate of liquid in molding step B (s ⁻¹)	TPC Temp. in Step B	Process Time Available (s)	Total Molding Strain Achievable (L/D)
0.1	400 °C	1500	150
1.0	430 °C	900	900
10	450 °C	600	6000

Accordingly, to utilize the thermoplastic processing window, it is important to control the temperature history of the alloy during processing at a constant strain rate. Further, to ensure the best possible casting, the thermoplastic forming should be completed before the temperature falls below the minimum critical temperature for instability (Table I). Equivalently, forming should be completed before the pressure necessary to maintain the injection velocity rises above the critical value. The factors that need to be balanced for each step of the process are summarized below in Table III.

Table III: TPC Process Steps

Step	Temperature	Pressure Control	Strain Rate	Process Time
Step A: Quenching	Start: above T_m End: TPC zone $T_{nose} > T > T_g$.	Pressure used to move melt through gates and tooling into mould is ≤ 10 MPa.	Strain rate not to exceed critical value determined by FIG. 6. Preferred ~ 10 to 100.	Avoid crystallization during Quenching Step. Cooling rate determined by TTT- diagram (i.e. crystallization time, t_x , at T_{nose}).
Step B: TPC Moulding	Start and maintain: $T_{nose} > T > T_g$	Pressure must remain below critical value to avoid melt instabilities and wear on die tooling preferred ~ 10 MPa or less but must be adequate to mould part.	Strain rate used for thermoplastic moulding of component should not exceed critical strain rate at given moulding temperature, See FIG. 6. Typical rates of 0.1 to 10 per s.	Process time available determined by TTT-diagram. Must avoid onset of crystallization or onset of phase separation. Required time determined by total strain required to mold part.
Step C: Final Chill	Start: $T_{nose} > T > T_g$ Ends at or near ambient. Temperature or T $\ll T_g$	Pressure drops to ambient.	No strain rate moulding has been completed.	Minimize time to minimize overall cycle time.

The method according to the invention then comprises several key features, including: (1) control of the liquid alloy flow; (2) control of the temperature history of the alloy during casting/forming; and (3) control of the turbulence of the alloy during flow and processing.

In one embodiment of the invention, for the control of the liquid alloy flow, the liquid velocity and the strain rate are controlled during the injection of the

1 alloy into the die. This liquid flow should be correlated with the liquid
temperature history to ensure proper forming "time". In this step, the injection
rate as well as the injection pressure should be monitored. By carefully
5 monitoring these parameters, proper laminar or Newtonian flow of the liquid can
be maintained and turbulence can be avoided, thereby preventing instabilities to
the melt front, gas entrainment in the alloy due to cavitation, and the
subsequent elimination of porosity, and inhomogeneities such as shear banding
or atomization.

10 In a preferred embodiment of the invention, the temperature history of
the liquid should also be controlled both during injection and forming of the
component. This control allows sufficient time for forming and shaping the
component at low pressures and low injection rates while maintaining a stable
15 laminar flow regime. By carefully monitoring these temperature parameters,
the invention allows for large overall plastic strains prior to freezing, allows
replication of fine detail by increasing the available time prior to part freezing,
and permits long and narrow section fabrication.

20 Although the above are the basic components of the thermoplastic casting
method according to the current invention, additional parameters will be
discussed with respect to alternative embodiments of the thermoplastic casting
method and apparatus according to the invention.

25 One simplified embodiment of the thermoplastic casting apparatus
according to the invention is shown in schematic cross-section in FIG. 7. The
apparatus 10 generally comprises a gate 12 in liquid communication between a
reservoir 14 of molten liquid amorphous alloy and a heated mould 16. In such
30 an embodiment, the liquid flows through the gate at a temperature $T_{L,0}$ near the
melting temperature of the alloy. When the molten alloy contacts the mould it
begins to cool as shown for Step A in FIGs. 2 and 3. The molten alloy is rapidly
cooled past the critical crystallization temperature T_{nose} , but is stabilized above
the glass transition temperature, T_g , by the heated mould, which is held at a
35 temperature $T_{M,0}$. By heating the mould, the relaxation of the liquid alloy
temperature to the mould temperature is extended. As shown in FIG. 8, the

1 liquid alloy temperature will relax exponentially to the mould temperature with
a time constant τ_v .

5 For example, FIG. 9 shows plots of a conventional amorphous alloy cold
casting method in comparison with a heated mould thermoplastic casting process
according to the current invention. In the conventional cold mould method, the
alloy is rapidly cooled below the glass transition temperature. While such a
process ensures that the alloy will not undergo crystallization, the processing
10 time available is greatly reduced, limiting the types of parts that can be made
and also requiring the use of high-speed injection molds to ensure sufficient alloy
material is placed into the mould prior to solidification.

15 Although so far only experimentally determined temperature histories
have been discussed, it should be understood that the temperature history of a
liquid alloy can be determined prior to processing by solving the Fourier heat
flow equation for the liquid alloy at some initial temperature injected into a
mould at some other initial temperature, such as in the apparatus depicted in
FIG. 7. (See, W.S. Janna, *Engineering Heat Transfer*, p. 258, the disclosure of
20 which is incorporated herein by reference.) By solving the fundamental process
inequalities, and observing the fundamental time scales, practical and
measurable process parameters such as size and complexity of a castable piece
may be determined.

25 For example, the process conditions for the material Vitreloy-1 can be first
estimated theoretically and a temperature history produced. The result of one
such calculation is shown schematically in FIG. 3. In this example, the thermal
conductivity of liquid Vitreloy-1 (K_v) is 18 Watts/m-K; the thermal conductivity of
30 a exemplary copper mould (K_M) is 400 Watts/m-K; the specific heat (C_p) of
Vitreloy-1 (@ 500 °C) is 48 J/mole-K or 4.8 J/cc-K; and the molar density of
Vitreloy (ρ) is 0.10 cc/mole. Given such values, the thermal diffusivity of
Vitreloy-1 can be expressed as $K_v/C_p = 0.038 \text{ cm}^2/\text{s}$. We can assume that the
35 thermal diffusivity of the mould is much greater than the liquid Vitreloy.
Accordingly, the thermal relaxation time of the liquid alloy in the mould can be
roughly given by the equation:

$$\tau_v = D^2/4K_v, \quad (1)$$

where D is the thickness of the moulded part.

Assuming no thermal impedance at the mould/liquid alloy interface, i.e., no shrinkage gap, for a part thickness of 1.0 cm, the thermal relaxation time of the liquid alloy is about $\tau_v = 6$ s. Using this number it is clear that at a temperature of 450 °C there is an available process time (according to Table II) of about 500 seconds. Accordingly, using a heated copper mould, there is ample time to process the alloy under near isothermal conditions at strain rates as high as 10 s⁻¹, under homogeneous Newtonian flow conditions, and near isothermal conditions in the liquid. Given these conditions, a total strain of about 5000 could be achieved to produce a plate a total of about 25 meters long. As a result, batch or even continuous sheets of metallic glass can be produced.

It should be understood that the above process is best performed under near isothermal conditions with the molten liquid in Step B, and the analysis used here applies only to cases approaching isothermal conditions. Under these conditions, the sample behaves as a uniform fluid. If temperature gradients are present in the liquid, which flows in the mold during Step B, the flow will be inhomogeneous and the analysis is more complicated.

By comparison to the calculated values above, FIG. 10 shows a measured TTT-diagram for Vitreloy 1. In this diagram, T_m is the alloy melting temperature (liquidus), T_x is the crystallization temperature (at the "nose"), T_g is the glass transition temperature (defined as the temperature where the viscosity of the alloy is 10¹² Pas-s), and T_{nose} is the point at which the time to onset of crystallization is at a minimum, here about 60 seconds.

The relationship between T_{nose} and the critical casting thickness and the critical cooling rate for a glass forming alloy can be determined, as above, from the solution of the heat flow equations for a cylinder and a plate. (See, W.S. Janna, *Engineering Heat Transfer*, p. 258, the disclosure of which is incorporated herein by reference.) In these calculations, we assume the mould has a

temperature at T_g , and the initial molten alloy has a temperature, T_i , equal to $(T_m + 100^\circ\text{C})$. Assuming again that the mould has a high thermal conductivity (e.g., molybdenum or copper), one can obtain the following relationships for a plate of total thickness L :

$$t_x = t(T_{\text{nose}}) = 2.4 \text{ (s/cm}^2\text{)} \times L_{\text{crit}}^2 = 60 \text{ s (for Vitreloy-1)}$$

$$R_{\text{crit}} = 42 \text{ (Kcm}^2\text{/s)/}L_{\text{crit}}^2 = 1.7 \text{ K/s (for Vitreloy-1),}$$

and for a cylinder of diameter D :

$$t_x(T) = T_{\text{nose}} = 1.2 \text{ (s/cm}^2\text{)} \times D_{\text{crit}}^2 = 60 \text{ s (for Vitreloy-1)}$$

$$R_{\text{crit}} = 84 \text{ (Kcm}^2\text{/s)/}D_{\text{crit}}^2 = 1.7 \text{ K/s (for Vitreloy-1),}$$

where L_{crit} and D_{crit} are the critical casting dimension parameters in centimeters below which one obtains an amorphous alloy, R_{crit} is the critical cooling rate to obtain glass in Kelvin per seconds, and t_x is the critical minimum time to crystallization at the temperature T_{nose} . Utilizing these relationships, it is possible to convert a critical casting thickness into a minimum crystallization time, t_x , or to a minimum critical cooling rate for producing an amorphous object.

In relation to FIG. 8, above, we can define a thermalization time, τ_t , as the time required for the temperature of an alloy melt to relax from the initial melt temperature, close to ($\sim 90\%$) of the way, to a final mould temperature (T_M). This is also the time scale to achieve a uniform temperature in the liquid layer. More specifically, after $2 \times \tau_t$, there is only 1% temperature variation in the molten alloy liquid. Accordingly, the centerline temperature will follow a time dependence according to Equation 2, below.

$$T(t) = T_M + \Delta T e^{-\psi t} \quad (2)$$

where the thermalization time $\tau_t = \ln(10)\tau$, and the thermal diffusivity of the liquid is (κ in cm^2/s) = $0.038 \text{ cm}^2/\text{s}$ (for Vitreloy-1). This can of course be adjusted for other materials. Again from the solution of the heat flow equation the following thermalization times are obtained for a Vitreloy-1 plate of thickness, L :

$$\tau_T = 0.25 L^2/\kappa = 6.6 \text{ (s/cm}^2\text{)} \times L^2,$$

and for a Vitreloy 1 cylinder of diameter, D:

$$\tau_T = 0.12 D^2/\kappa = 3.1 \text{ (s/cm}^2\text{)} \times D^2.$$

For example, a 1 cm thick plate of Vitreloy 1 has a τ_T of 6.6 seconds. (It should be noted that the thermalization temperature is relatively independent of the initial and mould temperatures.)

A minimum mould time τ_M for molding a particular component can also be determined from these equations. The minimum time required to mold an object or shape can be defined in several ways. The total strain ϵ_{tot} that the liquid must undergo to form the part could be determined. This is equal to the greatest aspect ratio of the part. For example, a plate of length s and thickness L will require a total strain of $\epsilon_{tot} \sim s/L$. Accordingly, if the strain rate during molding is ϵ_t , then the molding time may be found according to Equation 3, below.

$$(\epsilon_{tot}/\epsilon_t) = \tau_M. \quad (3)$$

Alternatively, the molding time might be determined in terms of the time required to fill a mould with liquid injected at some volumetric rate (volume/s). For instance, if liquid is injected through a gate into a mold cavity, we must fill the mold cavity to produce the component. If V is the volume of the mold cavity and dv/dt is the injection rate, then the molding time can be expressed according to Equation 4, below.

$$\tau_M = V/[dv/dt] \quad (4)$$

Using the above Equations, it is possible to write down the fundamental inequalities for the thermoplastic casting process. In Step A, the initial quench step, the temperature is lowered from $T_{melt} + \Delta T_{overheat}$, to $T_{mould} = T_g + \Delta T_{mould}$. This occurs in a processing time, τ_A . This time is equal to the time that it takes for liquid alloy to move through the "A" stage of the TPC process. In most cases the following inequalities are required for the Step A process:

$$\tau_T < \tau_A < t_X \quad (I)$$

As will be discussed later, the use of a heat exchanger will reduce τ_T , allowing for a shorter τ_A . In fact, τ_T is directly related to the individual "channel thickness" D shown in FIG. 7, in Step A (multiple channels can be used in parallel). Although inequality (I) is required for most embodiments, it should be understood that a heat exchanger with small channel dimensions may well enable Step A to be successfully carried out when it would not otherwise be possible to satisfy the inequality in (I).

In Step B, the molding/shaping step, the sample is formed into a net shape. This may be a rod, plate, tube, or another more complex shape (e.g. cell phone or watch case). This step is accomplished in a time scale τ_B at a target temperature T_B . This time scale should satisfy the following inequality:

$$\tau_M(T_B, \dot{\epsilon}_t) < \tau_B < \tau_X(T_B) \quad (II)$$

Here the time scales τ_M and τ_X depend explicitly on the temperature T_B , and on the strain rate ($d\epsilon/dt = \dot{\epsilon}_t$) at which the process is carried out. All other variables (e.g. the pressure gradient required to maintain the strain rate) are determined by T_B and $\dot{\epsilon}_t$. Thus, these parameters can be taken as the two independent process variables. Equivalently, we could use pressure P and temperature T_B as controlled variables (with $\dot{\epsilon}_t$ determined from these).

As an example, in the case of Vitreloy 1, if $\dot{\epsilon}_t = 1 \text{ s}^{-1}$, and the temperature T_B is chosen to be $\sim 80 \text{ C}$ above T_g , or T or $T_B = 700 \text{ K}$ (427 C), we find $\eta(T) = 2 \times 10^7 \text{ Pas-s}$, as shown in FIG. 11. From this value of viscosity, we can determine the pressure gradient required to maintain the strain rate using standard solutions to the Stokes equation, and τ_M can then be related to the basic processing parameters. For example, to fill a mold of length S and thickness L requires a total strain $\epsilon_{tot} = S/L$, and a total time $\tau_M = L/(S \dot{\epsilon}_t)$. The pressure required to achieve the assumed strain rate depends on the alloy viscosity at temperature T_B , which can also be computed, as shown in FIG. 11.

1 Although the apparatus shown in FIG. 7, and discussed above is a
simplified version of the invention, it should be understood that several features
can improve the operation of such an apparatus including: (1) inverted (counter-
5 gravity) liquid injection; (2) controlled gas atmosphere or vacuum environment
within melting injection and mould systems; and (3) continuous melt supply, i.e.,
repetitively filled moulds.

Each such alternative embodiment has at least one advantage. The
inverted liquid injection prevents gas entrainment and pore formation, the
10 controlled gas atmosphere prevents oxidation of the liquid alloy during the
process, and the continuous melt enables rapid throughput and controlled
viscosity and injection characteristics of the liquid.

In FIG. 3 a TTT comparison of a Vitreloy-1 material versus a marginal
15 amorphous alloy is shown. Because of the marginal glass properties of the non-
Vitreloy alloy, the length of time available to process the marginal amorphous
alloy is greatly reduced. Accordingly, it is necessary to reduce the temperature
of the alloy more rapidly to bypass crystallization at the T_{nose} . As a result, it
20 would seem to be impossible to create pieces having the same dimensional sizes
as those made with the more processable Vitreloy-1 alloy material.

FIG. 12 shows a modification of the basic TPC apparatus that makes such
larger dimensioned plates and pieces, possible. Specifically, FIG. 12 shows an
25 alternative embodiment of the invention directed to an apparatus for increasing
the critical casting thickness of glass forming alloy plates using an expander
region in the mould. As in the conventional TPC apparatus, the expander TPC
apparatus 20 shown in FIG. 12 also contains a gate 22 in fluid communication
30 between a reservoir 24 of molten liquid alloy material and a heated mould 26.
However, the heated mould has a region of expanded dimension 28, which
enlarges the dimensional size of the cast plate (Step B) once the alloy has been
rapidly cooled past the critical "nucleation or crystallization nose" (Step A). This
35 expander zone 28 allows for the casting of amorphous alloy plate sections of
much greater dimensional thickness than would be possible in a single size

1 mould. The cast piece 30 then enters a chiller 32, which rapidly freezes the final
metal plate 34 article to ambient temperature (Step C).

5 In the plate extrusion, expander, and related thermoplastic casting
apparatuses discussed above, special attention needs to be paid to the boundary
between the die tools and the undercooled liquid. Particularly, it is important to
control the behavior of the flowing liquid at the interface. In short, the interface
can either be non-slipping or slipping depending on the friction between the die
and melt. To be non-slipping the surface of the mould must have a specified
10 level of traction according to Equation 45, below.

$$\tau \sim \eta \frac{V_{\max}}{d} \quad (5)$$

15 where τ is the traction, η is the liquid viscosity, V_{\max} is the melt velocity field for
non-slip boundary, and d is the size of the flow path. As shown schematically in
FIG. 13, the maximum velocity, V_{\max} , of the melt is found at the center of the
melt away from the walls of the mould. In turn, the liquid viscosity, η , during
20 Step B of the process is determined by the TPC process map conditions (viscosity
depends on mould temperature etc., as is shown graphically in FIG. 11). This
property then determines the minimum static friction coefficient required to
maintain no-interfacial slip, according to Equation 6, below.

$$\mu > \eta \frac{V_{\max}}{Pd} = \eta \frac{\epsilon \dot{\gamma}}{P} \quad (6)$$

30 where μ is the frictional coefficient, P is the pressure, and $\epsilon \dot{\gamma}$ is the strain rate.

The friction coefficient, μ , can be controlled by surface roughness of the die
tool, and/or by use of die lubricants, etc. For example, to maintain non-slip
conditions, such that the liquid alloy continues to interact with the walls of the
35 dies, the surface must be sufficiently rough. The die tool surface roughness can
be controlled to achieve this, e.g., a polished die tool section can be used if a low μ
and interfacial slip/sliding, etc. is desired. For example, for plate extrusion it is

1 desirable that the interface slip before the melt leaves the tool. This slipping at
the end of the casting prevents "melt bulge" in the extruded sheet - improving
the quality of the sheet. Accordingly, in such an embodiment the last section of
5 the extrusion tool could be polished to optimize high quality sheet production.

FIG. 14 shows a detailed view of the expander region of the heated mould.
In the TPC expander described earlier in FIG. 12. In such an embodiment, an
interfacial slip is not desired since the metal should "bulge" into the expanded
region. Accordingly, the tools should be roughened in the "expansion zone". With
10 a no slip condition, the melt will "bulge" into the "expanded zone", and a thicker
sheet will be formed. In fact, the "bulging" will occur at a certain rate as the
liquid passes through the "expansion zone". To prevent slip, the expansion zone
must be tapered so that "bulging" keeps up with melt flow to maintain the non-
15 slip condition. For example, preferably the expansion zone surface 40 has a
specified "rms roughness" 42 with an expansion "pitch" angle 44 less than about
10 degrees to about 5 degrees, such as is described in FIG. 14. Additionally, the
expander apparatus may preferably have accurate mould temperature control,
20 such as a feedback control loop, control of the melt injection temperature, control
of the liquid injection velocity, and control of the maximum pressure for a given
injection velocity.

Although the discussion thus far has focussed only on the use of TPC to
25 form pure amorphous alloy materials, the TPC method can be used to fabricate
composite materials with "tailored" properties. This can be accomplished by
"mixing" a solid phase with a glass forming liquid in the initial stages of TPC
processing and consolidating the mixture into a "net shape" in the final stages of
30 processing. TPC composite manufacturing could be used to make rods, plates,
and other net-shaped parts. For example, such a process could be used in the
continuous manufacture of composite penetrator rod stock.

One example of an apparatus 50 for TPC composite manufacturing is
shown in FIG. 15. In this embodiment, a solid powder 52, such as a reinforcer is
35 mixed with the liquid alloy 54 in a mixer/agitator 56 prior to flowing into the
gate 58. A screw feed mechanism 60 is utilized to ensure that the alloy is feed

1 into the gate at the proper rate. Once in the gate the apparatus is identical to
that described in FIG. 7, above. Utilizing the mixer, a composite alloy material
can be produced in either batch or continuous feed processes. It is preferred in
5 such an embodiment that there be precise control of the volume fraction of the
reinforcer powder, precise control of the size distribution of the reinforce
powder, and minimal reaction between the matrix/reinforcement due to limited
process times at relatively low temperatures.

10 In yet another alternative embodiment, a TPC wire and/or braided cable
apparatus 70 is shown schematically in FIG. 16. In this embodiment, a liquid
alloy 72 is fed through a gate 74 into a heated mould 76. However, the mold
comprises a plurality of channels 78 designed to divide the alloy flow such that a
multiplicity of hot flows of liquid alloy are fed through the hot mold to form
15 individual braids 80 of a wire or cable. These individual strands are then
braided in a braiding apparatus 82 held at the moulding temperature, and then
the braided wire 84 is chilled to ambient temperature to form a multi strand
wire or cable in the chiller 86. Utilizing such an apparatus, cables and wires of
20 various dimensions and properties can be formed.

Finally, a more detailed depiction of an extrusion die tool 90 for forming
continuous sheets of material is shown schematically in FIG. 17. This
embodiment shows in more detail the melting stage 92, the heat exchanger 94,
25 the injector 96, and the die tool 98. Although any suitable melting stage capable
of maintaining an initial melt temperature and an initial injection pressure may
be used, the simple embodiment shows a container 100 having an RF heating
temperature control 102 and a column height pressure controller 104. In
30 another embodiment, the melting stage may also comprise a pre-treatment stage
for soaking the melt, and a stirring device for ensuring an isothermal melt.

Likewise, although any suitable heat exchanger can be used for the
quenching stage, the quenching stage 94 shown in more detail in FIG. 18
35 includes a combination of conduction and convection flow patterns to achieve
adequate quenching and to avoid the crystallization nose of the material. For
example, the exemplary embodiment of the heat exchanger 94 shown in FIG. 18

1 has an active cooler 106, and utilizes narrow flow channels and shaped fins 108
to promote heat exchange by a combination of conduction and convection to
rapidly cool the alloy below the nose temperature. The heat exchanger is also
5 provided with a thermocouple 110 to sense the temperature and a cold gas flow
for the active control of the temperature.

Finally, any injector suitable for controllably feeding the liquid alloy into
the die tool may be utilized. In the exemplary embodiment shown in FIG. 17, the
10 injector 96 is a control screw drive 112 where rotation frequency, control pitch,
and screw compression can be utilized to achieve the desired pressure and flow
velocity in the injector. A flow meter can be connected to a computer feedback
control 114 to control these parameters. Such a computer control can also
15 control the pressure and temperature of the melt stage, the temperature of the
heat exchanger, and the injector speed, thereby actively maintaining the process
within the thermoplastic process window required during Steps A and B.

The use of a heat exchanger to actively control the quench temperature of
the liquid alloy can also be utilized to expand the critical casting thicknesses of
20 the material. For example, an analysis was conducted on the cooling profiles for
a 5 mm thick liquid layer of the Vitreloy-106 material, the TTT diagram of which
is shown in FIG. 5, based on the solution of the material's heat flow equation.
This analysis determined that for a 5.0 mm thick slab of Vitreloy-106, heat
25 conduction only gives 6.9 s for the centerline temperature, T_c , to drop to 0.1 of
the initial temperature, where $\Delta T = T_{\text{initial}} - T_{\text{mould}}$. If the initial temperature,
 $T_{\text{initial}} = 1200\text{K}$, and the temperature of the mould, $T_{\text{mould}} = 673\text{ K}$, then at 6.9 s the
centerline temperature is 726 K, and at 13.8 s the centerline temperature is 678
30 K. The cooling rate average during the initial 6.9 s is $(527\text{K}/6.9\text{s}) = 76\text{ K/s}$.
However, while "passing the nose" at 900 K, the alloy has a critical cooling rate
of $(300\text{ K}/2.4\text{s}) = 125\text{ K/s}$. Accordingly, ambient cooling will not allow for the
production of an amorphous material in this example.

35 Similarly, the following formulas can be derived from solutions to the heat
flow equation for a cylinder and a plate of liquid alloy cooled by simple heat
conduction in a thick mould. The formulas assume that the thermal conductivity

of the mould is at least ~10 times that of the liquid alloy. In the equations, T_1 is the liquidus temperature of the alloy, κ is the thermal diffusivity of the alloy $\kappa = K_t/C_p$, K_t is the thermal conductivity of the mould in Watts/cm-K (exemplary values for K for typical mould materials such as copper and molybdenum are $K_{Cu} = 400$ Watts/m-K and are $K_{Mo} = 180$ Watts/m-K), and C_p is the specific heat of the alloy (per unit volume in J/cc-K). The cooling rate is related to the sample dimensions (plate thickness L , cylinder diameter D - in cm), by using the cooling rate at the mid-line of the sample (plate center or cylinder center) when the temperature of the centerline passes from $0.85T_1$ to $0.75T_1$. This is the location of the "nucleation nose" for a sample with a reduced glass transition temperature, $T_g/T_1 = 0.6$ (typical of good glass formers). The result is relatively independent of the mould temperature. It is also relatively independent of the details of the glass forming alloy (e.g. T_g/T_1). With these assumptions, the critical cooling rate can be related to the critical casting thickness as follows:

$R_{crit}^{plate} = \text{critical cooling rate (K/s)} = 0.4\kappa T_1/L_{crit}^2 = 0.4K_t T_1/(C_p L_{crit}^2)$ for a plate of thickness L .

$R_{crit}^{cyl} = \text{critical cooling rate (K/s)} = 0.8\kappa T_1/D_{crit}^2 = 0.8K_t T_1/(C_p D_{crit}^2)$ for a cylinder of diameter D .

For example, for Vitreloy 1, $K=0.18$ Watts/cm-K, $C_p = 5$ J/cm³-K, $T_1 = 1000$ K, we then have:

$R_{crit}^{plate} \approx 15/L^2$ (L in cm) \Rightarrow with a critical cooling rate of 1.8 K/s $D_{crit} = 2.9$ cm.

$R_{crit}^{cyl} \approx 30/D^2$ (D in cm) \Rightarrow with a critical cooling rate of 1.8 K/s, $D_{crit} = 4.1$ cm.

Critical cooling rates of various alloys estimated from sample relations using thermo-physical properties of Vitreloy-1 (a good approximation in general), are shown below in Table IV.

Table IV: Critical Cooling Rates

Alloy	Experimental Casting Thickness (cm)		Critical Cooling Rates
	Cylinder	Plate	
Vitreloy 1	4.1 cm ^c	2.9 cm	1.8 K/s ^m
Vitreloy 101	0.35 cm ^m	0.25 cm	247 K/s ^c
Vitreloy 4	1.2 cm ^m	0.9 cm	21 K/s ^c 26 K/s ^m
Vitreloy 106a	1.9 cm ^c	1.35 cm	7 K/s ^m
Fe-based glass	0.35 cm ^m	0.25 cm	247 K/s ^c
Ni-based Glasses	0.3 cm ^m	0.21 cm	340 K/s

(c = calculated) (m = measured)

The use of heat exchangers to expand the critical casting thicknesses can also be modeled using a theoretical TTT-curve, a rheology based on Vitreloy-1, and assuming a heat exchanger structure with 1 mm channels as shown in FIG. 18. The TTT-curves of various alloys can be estimated by shifting the time of the $t_{\alpha}(I)$ curve of the Vitreloy-1 TTT-diagram. In other words, a TTT-diagram of Vitreloy-1 or Vitreloy-106 (measured) can be taken, and a time scaling methodology used with the entire curve shifted in time by λt , where λ is the ratio of the time to the nose of the alloy to the time to the nose of Vitreloy-1.

Using these relations, to cast a 1 cm thick expanded plate, a 1 mm channel (channel width of 1 mm and "fin" width also 1 mm) expander is used and the material is then moved into an open 1 cm plate. The exchanger will reduce flow by a factor of $r_1 \sim 100$, unless compensated by an increase in casting pressure gradient. Accordingly, total casting pressure will be higher (~ 100 MPa). This can be done without penalty since flow instability in the exchanger will not reduce part quality (instabilities are damped in the final molding stage (e.g. open plate). Accordingly, a total strain of at least $\epsilon_{tot} \sim 10$ is needed to cast the 1 cm thick plate (in the open section). A factor of λ is lost in process time (at the TPC temperature). Thus, it is necessary to compare the total TPC strain available in Vitreloy-1 (TPC processing charts). For Vitreloy-101, for example, a total strain

1 of 10 must be attained in a time shortened by λ . The required condition for a
viable process (using available strain of 6000 in 600 s (Vitreylo 1) becomes:

$$5 \quad \epsilon_{\text{available}} = 6000 / \lambda = 6000 / 137 = 44 > \epsilon_{\text{tot}} = 10. \quad (7)$$

Which is achievable as shown in Tables I and II.

10 In conclusion, with 1 mm channels, cooling rates will be ~ 1000 K/s. Accordingly, a 1 cm thick plate of a Ni-base or Fe-base alloy can be cast using a
continuous casting method according to the present invention. Further, all the
alloys listed in Table IV become highly processable using the heat exchanger
methods of the present invention. Therefore, using an active heat exchanger
15 apparatus according to the embodiment of the present invention shown in FIGs. 17 and 18, the critical cooling rate is no longer a limitation for making
components with ~ 1 cm thicknesses. The method essentially provides a means of
"leveraging" the processability of metallic glass forming liquids allowing
enhancement of critical casting dimensions and opening a much wider range of
20 alloy compositions from which components can be fabricated.

It should be understood that although the above-discussion of TPC
apparatus have focussed on generic moulds and die tools, that any suitable
shaping tool may be utilized with the current invention. For example, closed-die
25 or closed-cavity dies, such as split-mold type dies may be used to make individual
components. Alternatively, open-cavity dies, such as extrusion die tools may be
used for continuous casting operations.

30 The invention is also directed to products made from the thermoplastic
casting process and apparatus described herein. For example, because of the
high-quality defect free nature of the TPC process, the method may be used to
produce components with submicron features, such as optically active surfaces.
Accordingly, micro or even nanoreplication is possible for ultra-high precision
35 components, i.e., products with functional surface features of less than 10
microns. In addition, the extended process times above, along with the near
isothermal conditions of TPC allow substantial reduction of internal stress

1 distributions in parts, allowing for the production of articles free of porosity, with
high integrity, and having reduced thermal stress (less than about 50 Mpa).
Such components may include, for example, electronic packaging, optical
5 components, high precision parts, medical instruments, sporting equipment, etc.
Preferably, the alloy comprising the end-product has an elastic limit of at least
about 1.5%, and more preferably about 1.8%, and still more preferably an elastic
limit of about 1.8 % and a bend ductility of at least about 1.0%, indicating
superior amorphous properties.

10 The preceding description has been presented with reference to presently
preferred embodiments of the invention. Workers skilled in the art and
technology to which this invention pertains will appreciate that alterations and
changes in the described structures and processes may be practiced without
15 meaningfully departing from the principal, spirit and scope of this invention.

Accordingly, the foregoing description should not be read as pertaining
only to the precise structures described and illustrated in the accompanying
drawings, but rather should be read consistent with and as support to the
20 following claims which are to have their fullest and fair scope.

1 WHAT IS CLAIMED IS:

1. A method of thermoplastically casting an amorphous alloy comprising the steps of:

5 providing a quantity of an amorphous alloy in a molten state;

cooling said molten amorphous alloy to an intermediate thermoplastic forming temperature above the glass transition temperature of the amorphous alloy at a rate sufficiently fast to avoid crystallization of the amorphous alloy;

10 stabilizing the temperature of the amorphous alloy at the intermediate thermoplastic forming temperature;

shaping the amorphous alloy under a shaping pressure at the intermediate thermoplastic forming temperature for a period of time sufficiently

15 short to avoid crystallization of the amorphous alloy to form a molded part; and

cooling the molded part to ambient temperature.

2. The method as described in claim 1, wherein the intermediate thermoplastic forming temperature is above the glass transition temperature of the amorphous alloy, but below a crystallization temperature (T_{NOSE}) of the amorphous alloy, where the crystallization temperature (T_{NOSE}) is defined as the temperature at which crystallization of the amorphous alloy occurs on the shortest time scale.

3. The method as described in claim 1, wherein the shaping pressure is low enough to maintain the amorphous alloy in a Newtonian viscous flow regime.

4. The method as described in claim 1, wherein the shaping pressure is from about 1 to about 100 MPa.

5. The method as described in claim 1, wherein the step of shaping includes the step of introducing the amorphous alloy into a heated shaping

1 apparatus is selected from the group consisting of a mould, a die tool, a closed
die, and an open-cavity die.

5 6. The method as described in claim 5, wherein the heated shaping
apparatus is kept at a temperature within about 150 °C of the glass transition
temperature of the amorphous alloy.

10 7. The method as described in claim 5, wherein the heated shaping
apparatus is kept at a temperature within about 50 °C of the glass transition
temperature of the amorphous alloy.

15 8. The method as described in claim 5, wherein the temperature of the
heated shaping apparatus is controlled through a temperature feedback
controller.

20 9. The method as described in claim 5, wherein the temperature of the
heated shaping apparatus is increased during the forming step.

25 10. The method as described in claim 5, wherein the amorphous alloy is
maintained in the heated shaping apparatus for a time suitable for the
amorphous alloy to reach a nearly uniform temperature substantially equal to
that of the heated shaping apparatus.

30 11. The method as described in claim 5, wherein the amorphous alloy is
introduced into the heated shaping apparatus at a specified flow rate, and
wherein the rate of flow of liquid alloy through the heated shaping apparatus is
maintained at one of either a constant velocity or a constant strain rate.

35 12. The method as described in claim 11, wherein the strain rate is
between about 0.1 and 100 s⁻¹.

13. The method as described in claim 5, wherein an applied pressure is used to move the amorphous alloy through the heated shaping apparatus.

14. The method as described in claim 13, wherein the applied pressure is less than about 100 MPa.

15. The method as described in claim 13, wherein the applied pressure is less than about 10 MPa.

16. The method as described in claim 1, wherein the shaping step takes about 10 to 100 times longer than the cooling step.

17. The method as described in claim 1, wherein the shaping step takes about 5 to 15 times longer than the cooling step.

18. The method as described in claim 1, wherein the shaping time is between about 3 and 200 seconds.

19. The method as described in claim 1, wherein the shaping time is between about 10 and 100 second.

20. The method as described in claim 1, wherein the shaping pressure is about 5 to 15 times more than the pressure applied to the molten amorphous alloy in the cooling step.

21. The method as described in claim 1, wherein the shaping pressure is about 10 to 100 times more than the pressure applied to the molten amorphous alloy in the cooling step.

1 22. The method as described in claim 1, wherein the shaping pressure
is about 50 to 500 times more than the pressure applied to the molten
amorphous alloy in the cooling step.

5 23. The method as described in claim 1, wherein the step of shaping the
amorphous alloy further comprises introducing the front end of the cooled
amorphous alloy into a dog-tail tool, which may be utilized to extract the molded
part continuously.

10 24. The method as described in claim 1, wherein the amorphous alloy is
a Zr-Ti alloy, where the sum of the Ti and Zr content is at least about 20 atomic
percent of the composition of the amorphous alloy.

15 25. The method as described in claim 1, wherein the amorphous alloy is
a Zr-Ti-Nb-Ni-Cu-Be alloy, where sum of the Ti and Zr content is at least about
40 atomic percent of the composition of amorphous alloy.

20 26. The method as described in claim 1, wherein the amorphous alloy is
a Zr-Ti-Nb-Ni-Cu-Al alloy, where sum of the Ti and Zr content is at least about
40 atomic percent of the composition of the amorphous alloy.

25 27. The method as described in claim 1, wherein the amorphous alloy is
an Fe-base alloy, where the Fe content is at least about 40 atomic percent of the
composition of the amorphous alloy.

30 28. The method as described in claim 1, wherein the amorphous alloy
may be described in general terms by the formula $(\text{Zr,Ti})_a(\text{Ni,Cu,Fe})_b(\text{Be,Al,Si,B})_c$, where a is in the range of from about 30% to 75% of the total
composition in atomic percentage, b is in the range of from about 5% to 60% of
35 the total composition in atomic percentage, and c is in the range of from about
0% to 50% in total composition in atomic percentage.

1 29. The method as described in claim 1, wherein the amorphous alloy is
 $\text{Zr}_{47}\text{Ti}_{13}\text{Ni}_{10}\text{Cu}_{7.5}\text{Be}_{27.5}$.

5 30. The method as described in claim 1, wherein the amorphous alloy
 has a supercooled liquid region (ΔT_{sc}) of about 30 °C or more, where ΔT_{sc}
 is defined as the difference of the onset of crystallization of the amorphous alloy
 (T_x) and the onset of glass transition of the amorphous alloy (T_g), as determined
10 from standard differential scanning calorimetry scans at 20 °C/min.

 31. The method as described in claim 30, wherein the supercooled liquid
 region (ΔT_{sc}) is about 60 °C or more.

15 32. The method as described in claim 30, wherein the supercooled liquid
 region (ΔT_{sc}) is about 90 °C or more.

20 33. The method as described in claim 1, wherein the amorphous alloy
 has a critical cooling rate of about 1,000 °C/sec or less, and the heat exchanger
 has a channel width less than about 1.5 mm. In another embodiment of the
 invention, the provided amorphous alloy has a critical cooling rate of about 100
 °C/sec or less, and the heat exchanger has a channel width less than about 5.0
25 mm.

 34. A method of thermoplastically casting an amorphous alloy
 comprising the steps of:

30 providing a quantity of an amorphous alloy at a melt temperature above
 the melting temperature of the amorphous alloy;

 pouring the amorphous alloy into a shaping apparatus at a flow rate and
 under a pressure to ensure laminar flow of the amorphous alloy, and
35 simultaneously cooling said amorphous alloy to an intermediate thermoplastic
 forming temperature above the glass transition temperature of the amorphous
 alloy at a rate sufficiently fast to avoid crystallization of the amorphous alloy;

1 stabilizing the temperature of the amorphous alloy at the intermediate thermoplastic forming temperature;

5 shaping the amorphous alloy to form a molded part, wherein the shaping occurs under a shaping pressure sufficiently low to avoid melt instabilities and wear on the shaping apparatus, at the intermediate thermoplastic forming temperature for a period of time sufficiently short to avoid crystallization of the amorphous alloy; and

10 cooling the molded part to ambient temperature.

35. The method as described in claim 34, wherein the shaping pressure at the intermediate thermoplastic forming temperature is sufficiently low to avoid wear on the shaping apparatus.

15 36. A thermoplastic casting apparatus for shaping an amorphous alloy comprising:

a reservoir of molten amorphous alloy;

20 a heated shaping tool; and

a gate in fluid communication between the reservoir and the heated shaping tool, wherein the heated shaping tool is held at a temperature such that molten amorphous alloy introduced thereto is cooled to an intermediate thermoplastic casting temperature above the glass transition temperature of the amorphous alloy sufficiently quickly to avoid crystallization of the amorphous alloy.

30 37. The thermoplastic casting apparatus as described in claim 36, wherein the heated shaping apparatus is selected from the group consisting of a mould, a die tool, a closed die, and an open-cavity die.

35 38. The thermoplastic casting apparatus as described in claim 36, wherein is an extrusion die capable of the continuous production of a two-dimensional amorphous alloy product.

39. The thermoplastic casting apparatus as described in claim 36, wherein the shaping tool is made of a material having a thermal diffusivity greater than that of the molten amorphous alloy.

40. The thermoplastic casting apparatus as described in claim 36, wherein the shaping tool is made of a material selected from the group consisting of copper, tungsten, molybdenum, an composites thereof.

41. The thermoplastic casting apparatus as described in claim 36, further comprising an injection system for injecting the molten amorphous alloy into the shaping tool.

42. The thermoplastic casting apparatus as described in claim 41, wherein the injection system is a counter-gravity injection system.

43. The thermoplastic casting apparatus as described in claim 36, further comprising an atmospheric controller for providing a controlled gas environment within at least a portion of the thermoplastic casting apparatus.

44. The thermoplastic casting apparatus as described in claim 43, wherein the atmospheric controller provides a vacuum environment within at least the shaping tool.

45. The thermoplastic casting apparatus as described in claim 36, wherein the shaping tool further comprises an expansion zone which includes:
a heat exchanger, designed to cool the molten amorphous alloy sufficiently rapidly to bring the temperature of the amorphous alloy below the crystallization temperature (T_{NOSE}), and

an expansion region having a thickness greater than that of the heat exchanger.

1 46. The thermoplastic casting apparatus as described in claim 45,
wherein expansion region has a thickness of from about 2 to 20 times the
thickness of the heat exchanger.

5 47. The thermoplastic casting apparatus as described in claim 36,
wherein the shaping tool has an entrance and an exit, and wherein the entrance
has a roughened surface designed to maintain contact between the shaping tool
10 and the molten amorphous alloy, and wherein the exit has a polished surface to
permit boundary slip between the shaping tool and the amorphous alloy.

15 48. The thermoplastic casting apparatus as described in claim 47,
wherein the exit is provided with a lubricant to promote slipping between the
shaping tool and the amorphous alloy.

20 49. The thermoplastic casting apparatus as described in claim 45,
wherein the expansion region has a roughened surface to designed to maintain
contact between the expansion region and the molten amorphous alloy.

25 50. The thermoplastic casting apparatus as described in claim 45,
wherein the expansion region has a pitch angle of less than about 60 degrees.

 51. The thermoplastic casting apparatus as described in claim 45,
wherein the expansion region has a pitch angle of less than about 40 degrees.

30 52. The thermoplastic casting apparatus as described in claim 36,
wherein the shaping tool is a split mould die.

35 53. The thermoplastic casting apparatus as described in claim 36,
further comprising a mixer in fluid communication between the reservoir and the
gate, and in further communication with a composite reservoir, said mixer being

1 designed to mix an additive material with the molten amorphous alloy to form a
composite alloy material.

5 54. The thermoplastic casting apparatus as described in claim 53,
wherein the additive material is a reinforcer.

10 55. The thermoplastic casting apparatus as described in claim 53,
wherein the mixer includes an agitator mechanism for ensuring homogeneous
mixing of the additive material and the molten amorphous alloy.

15 56. The thermoplastic casting apparatus as described in claim 53,
wherein the mixer includes a feeder mechanism to ensure that the composite
alloy material is introduced into the gate at a specified rate.

20 57. The thermoplastic casting apparatus as described in claim 56,
wherein the feeder mechanism is a screw feed mechanism.

25 58. The thermoplastic casting apparatus as described in claim 36,
further comprising a heated braiding apparatus in fluid communication with the
shaping tool, wherein the shaping tool comprises a mold having a plurality of
individual channels such that the molten amorphous alloy flows through the gate
into the plurality of individual channels to form a plurality of individual strands
of amorphous alloy, and wherein the plurality of individual strands of
amorphous alloy are then fed into the braiding apparatus, where the plurality of
30 individual strands are braided in to a single multibraid wire.

59. The thermoplastic casting apparatus as described in claim 58,
wherein the braiding apparatus is heated to the temperature of the shaping tool.

35 60. The thermoplastic casting apparatus as described in claim 36,
wherein the reservoir further comprises:

1 an heating temperature control for maintaining the temperature of the
molten amorphous alloy above the melting temperature of the amorphous alloy;
and

5 a column height pressure controller for controlling the pressure within the
reservoir.

61. The thermoplastic casting apparatus as described in claim 60,
wherein the reservoir further comprises:

10 a pre-treatment stage for soaking the melt; and

an agitator for stirring the molten amorphous alloy within the reservoir to
ensure an isothermal molten amorphous alloy.

15 62. The thermoplastic casting apparatus as described in claim 36,
further comprising a quenching stage in fluid communication between the gate
and the shaping tool for cooling the molten amorphous alloy to the intermediate
thermoplastic casting temperature prior to its entrance into the shaping tool to
20 form a cooled amorphous alloy.

63. The thermoplastic casting apparatus as described in claim 62,
wherein the quenching stage comprises a heat exchanger comprising a plurality
25 of narrow channels and fins for cooling the molten amorphous alloy by a
combination of conduction and convection.

64. The thermoplastic casting apparatus as described in claim 63,
30 wherein the heat exchanger further comprises a thermocouple in signal
communication with the heat exchanger and a temperature controller; the
temperature controller in signal communication with the heat exchanger to
control the temperature to which the molten amorphous alloy passing through
the quenching stage is cooled.
35

1 65. The thermoplastic casting apparatus as described in claim 62,
further comprising an injector for injecting the cooled amorphous alloy into the
gate at a specified rate.

5 66. The thermoplastic casting apparatus as described in claim 65,
wherein the injector is a screw drive feeder mechanism.

10 67. The thermoplastic casting apparatus as described in claim 66,
further comprising a computer control for controlling the speed of the screw drive
feeder mechanism.

15 68. The thermoplastic casting apparatus as described in claim 36,
further comprising a computer control for controlling at least one parameter of
the thermoplastic casting apparatus.

20 69. A metallic article with a substantially amorphous phase made by
the thermoplastic casting process described in claim 1.

25 70. The article as described in claim 69 wherein the article has a
minimum dimension of about 2 mm or more, and wherein the amorphous alloy
has a critical cooling rate of the about 1000 °C or more.

30 71. The article as described in claim 69 wherein the article has a
minimum dimension of about 5 mm or more, and wherein the amorphous alloy
has a critical cooling rate of the about 1000 °C or more.

35 72. The article as described in claim 69 wherein the article has a
minimum dimension of about 10 mm or more, and wherein the amorphous alloy
has a critical cooling rate of the about 1000 °C or more.

1 73. The article as described in claim 69 wherein the article has a
maximum critical casting thickness dimension of about 6 mm or more, and
wherein the amorphous alloy has a critical cooling rate of the about 100 °C or
5 more.

74. The article as described in claim 69 wherein the article has a
maximum critical casting thickness dimension of about 12 mm or more, and
wherein the amorphous alloy has a critical cooling rate of the about 100 °C or
10 more.

75. The article as described in claim 69 wherein the article has a
maximum critical casting thickness dimension of about 25 mm or more, and
wherein the amorphous alloy has a critical cooling rate of the about 100 °C or
15 more.

76. The article as described in claim 69 wherein the article has a
20 critical casting thickness dimension of more than about 20 mm, and wherein the
amorphous alloy has a critical cooling rate of the about 10 °C or more.

77. The article as described in claim 69 wherein the article has a
25 critical casting thickness dimension of more than about 50 mm, and wherein the
amorphous alloy has a critical cooling rate of the about 100 °C or more.

78. The article as described in claim 69 wherein the article has a
30 critical casting thickness dimension of more than about 100 mm, and wherein
the amorphous alloy has a critical cooling rate of the about 100 °C or more.

79. The article as described in claim 69 wherein the article comprises a
35 plurality of sections with an aspect ratio of about 10 or more.

1 80. The article as described in claim 69 wherein the article comprises a plurality of sections with an aspect ratio of about 100 or more.

5 81. The article as described in claim 69 wherein the article is selected from the group consisting of a sheet, plate, rode, and tube.

10 82. The article as described in claim 69 wherein the article is one of either a sheet or plate having a thickness of up to about 2 cm.

15 83. The article as described in claim 69 wherein the article is a tube having a diameter up to about 1 meter and a wall thickness of up to about 5 cm.

20 84. The article as described in claim 69 wherein the article has an elastic limit of more than about 1.5%.

25 85. The article as described in claim 69 wherein the article has an elastic limit of more than about 1.8%.

30 86. The article as described in claim 69 wherein the article has an elastic limit of about 1.8 % and a bend ductility of at least about 1.0%.

35 87. The article as described in claim 69 wherein the article has functional surface features of less than about 10 microns in scale.

40 88. The article as described in claim 69 wherein the article is selected from the group consisting of a watch case, a computer case, a cellphone case, an electronic product, a medical device, and a sporting d.

45 89. The article as described in claim 69 wherein the article has a thermal stress of less than about 50 MPa.

1 90. The article as described in claim 69 wherein the article is
substantially free of porosity.

5 91. The article as described in claim 69 wherein the article has a high
integrity.

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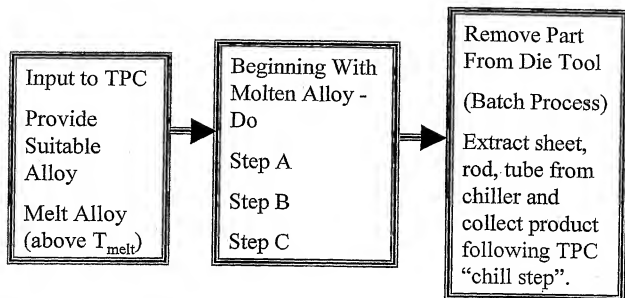
FIG. 1

FIG. 2

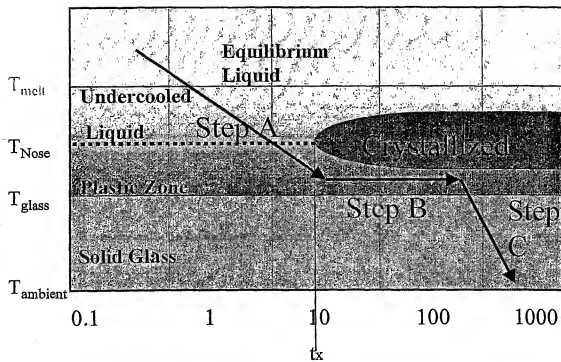


FIG. 3

Vitreloy 1 vs. Marginal Glass
Forming Alloys with
nucleation "nose" at ~6-7 sec.

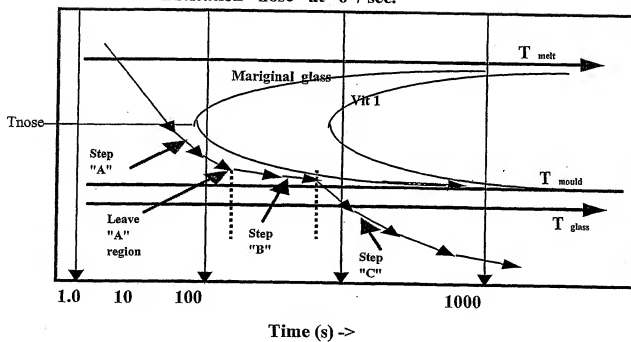


FIG. 4a

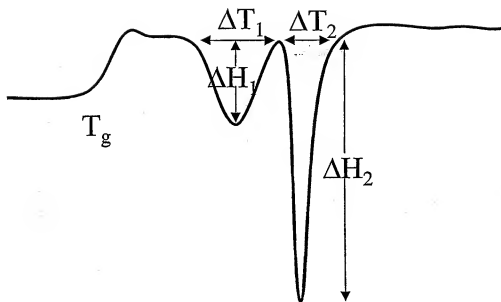


FIG. 4b

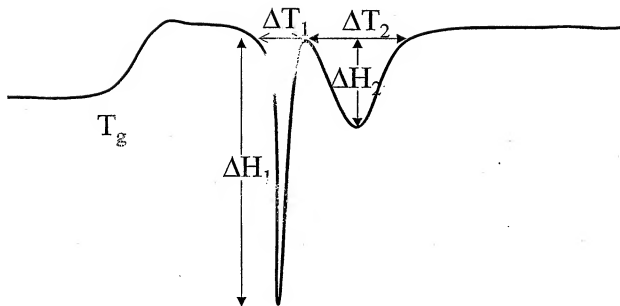


FIG. 5

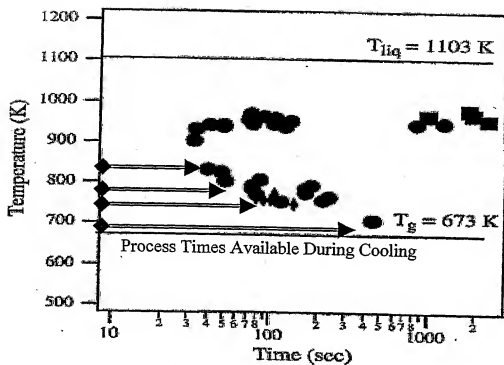


FIG. 6

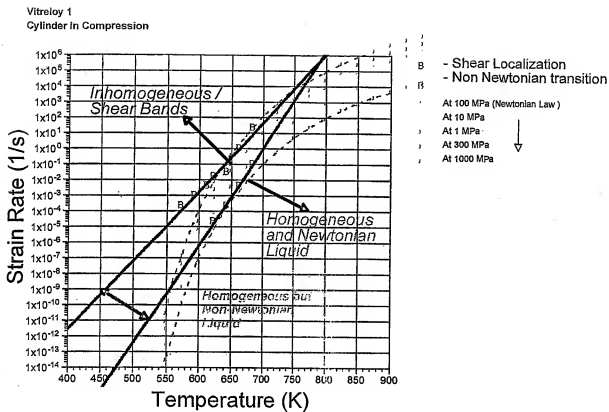
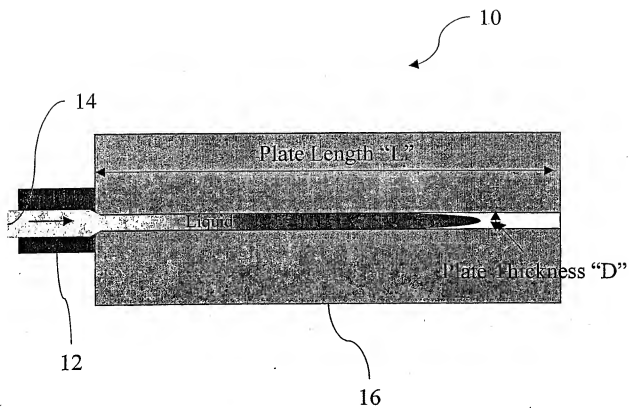


FIG. 7



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FIG. 8

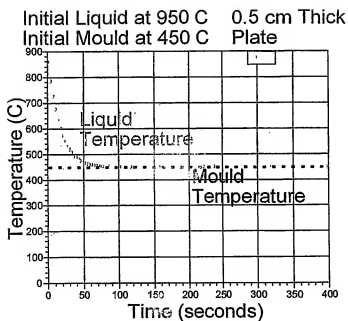


FIG. 9

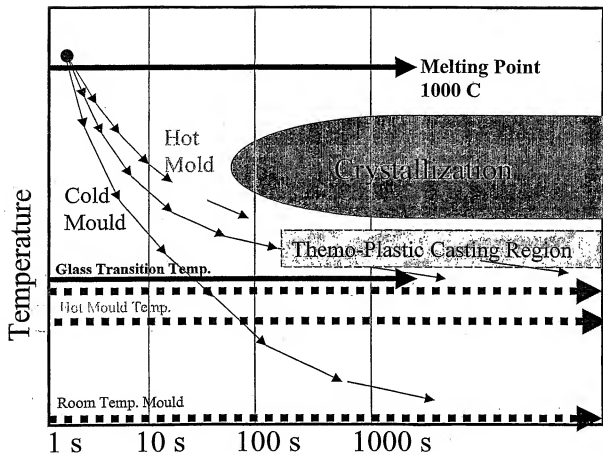


FIG. 10

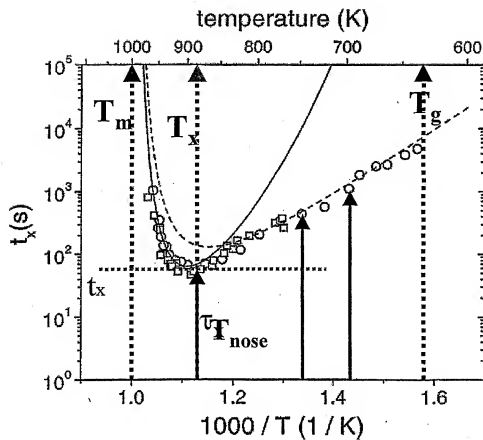
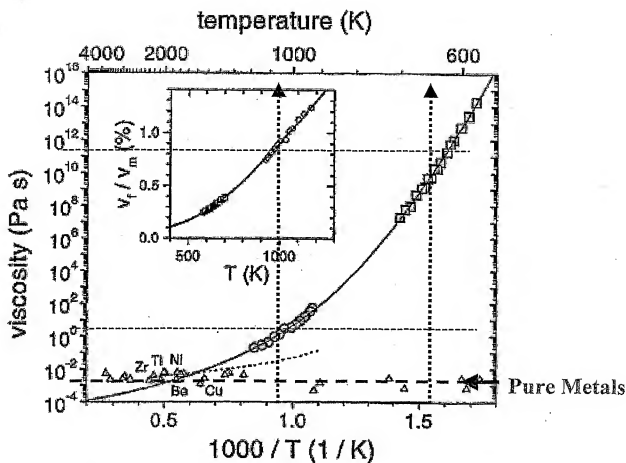


FIG. 11



Fit to data

$$\eta(T) = \eta_0 \exp[DT_0/(T-T_0)]$$

$$\eta_0 = 4 \times 10^{-5} \text{ Pas-s}$$

$$D = 18.5$$

$$T_0 = 412K$$

 $\leftarrow \dots T_{\text{melt}}$
 $\leftarrow \dots T_g$

FIG. 12

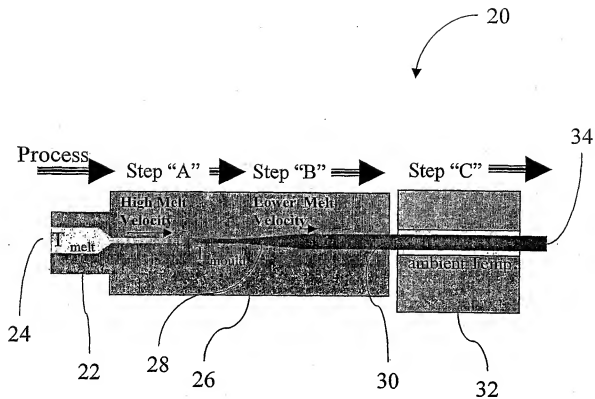


FIG. 13

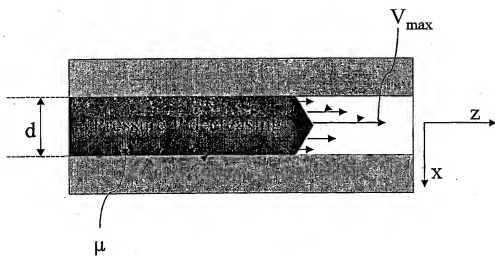


FIG. 14

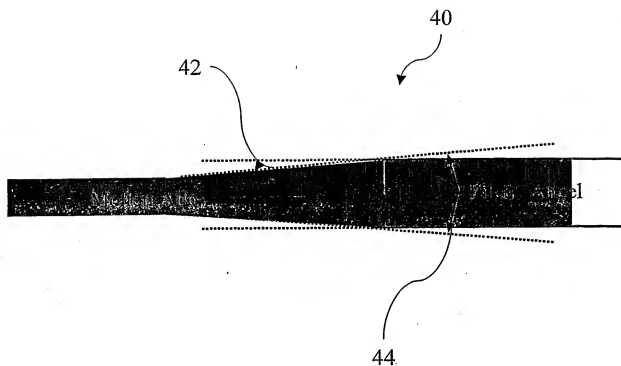


FIG. 15

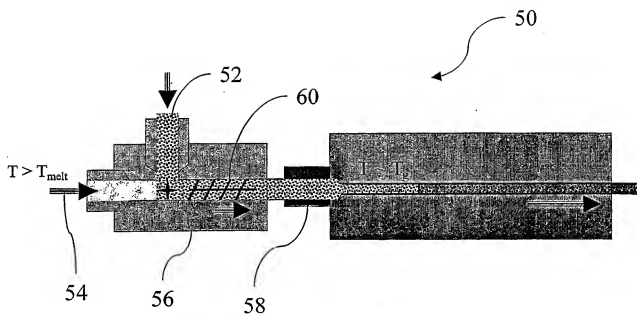


FIG. 16

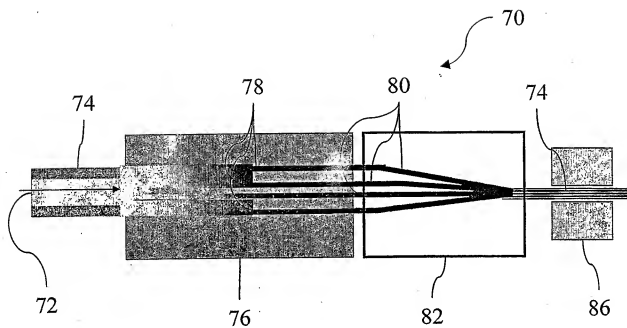


FIG. 17

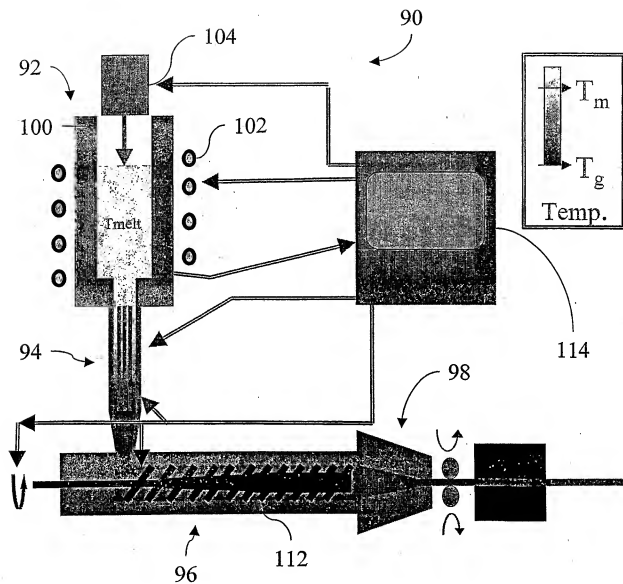
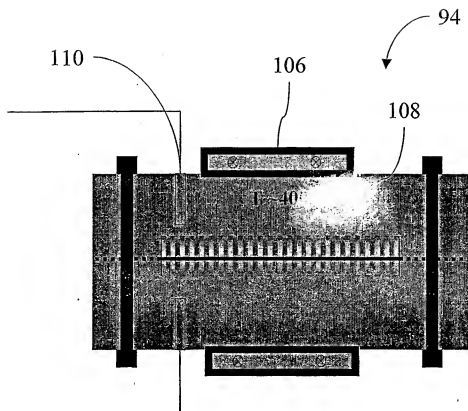


FIG. 18



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/03026

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B22D 11/00, 23/00, 27/04

US CL : 164/122, 348, 463, 423

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 164/122, 348, 463, 423

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EAST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,279,349 A (HORIMURA) 18 January 1994, col. 2, lines 48-54, abstract and figures 1-2.	1-44, 52-91
Y ✓	US 5,213,148 A (MASUMOTO et al.) 25 May 1993, entire specification and drawings.	1-44, 52-91
Y	US 5,896,642 A (PEKER et al.) 27 April 1999, col. 2, lines 17-21.	11, 12, 38
Y ✓	US 4,330,027 A (NARASIMHAN), 18 May 1982, abstract and figure 1.	53-57
Y	US 5,740,854 A (INOUE et al.) 21 April 1998, col. 1, lines 51-59.	70-78

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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- "O" document referring to an oral disclosure, use, exhibition or other means
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

26 June 2003 (26.06.2003)

Date of mailing of the international search report

17 JUL 2003

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